PB90-132572

International Symposium on Field Screening Methods for Hazardous Waste Site Investigations (1st), Proceedings Held in Las Vegas, Nevada on October 11-13, 1988

Life Systems, Inc., Cleveland, OH

Prepared for:

Environmental Monitoring Systems Lab., Las Vegas, NV

1988

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/D-89/189

2.

3. RECIPIENT'S ACCESSION NO. PB90 132572/AS

4. TITLE AND SUBTITLE
FIRST INTERNATIONAL SYMPOSIUM, FIELD SCREENING METHODS FOR HAZARDOUS WASTE SITE INVESTIGATIONS, SYMPOSIUM PROCEEDINGS

5. REPORT DATE

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Llewellyn R. Williams

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
U.S. Environmental Protection Agency, Environmental
Monitoring Systems Laboratory, Las Vegas, Nevada
89193-3478

10. PROGRAM ELEMENT NO.
Y105 H0301

11. CONTRACT/GRANT NO.
68-03-3511

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring Systems Laboratory, LV, NV
Office of Research and Development
U.S. Environmental Protection Agency
Las Vegas, NV 89193-3478

13. TYPE OF REPORT AND PERIOD COVERED
Proceedings

14. SPONSORING AGENCY CODE
EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The 1st International Symposium on Field Screening Methods for Hazardous Waste Site Investigation was held October 11-13, 1988, in Las Vegas, Nevada. Objectives of the meeting were to discuss available and developing technology for rapid, low-cost detection and monitoring of toxicants at hazardous waste sites; to address new opportunities for government/private cooperative ventures to develop and commercialize field monitoring technology; and to inform symposium delegates and scientists through open discussions, technical sessions, exhibits and peer-reviewed publications of new approaches to solve site-investigation problems. The scope of the symposium included portable and "fieldable" instrumentation, test kit technology, advanced field sampling methodology and support technology designed to enhance the cost effectiveness, speed and data quality of hazardous waste site investigations. This proceedings document presents about 90 technical papaers presented in the symposium. The wide variety of instruments discussed or exhibited at the symposium included portable versions of gas chromatographs, mass spectrometers, X-ray fluorescence spectrometers, Fourier transform IR spectrometers and ion mobility spectrometers. Chemical sensor technology, including the latest developments in optical fibers, coatings, and other materials advances, and immunochemical techniques for field screening kits and hybrid sensor arrays.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES 491

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB90-132572

First International Symposium

FIELD SCREENING METHODS FOR HAZARDOUS WASTE SITE INVESTIGATIONS

October 11-13, 1988

Symposium Proceedings

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

FIRST INTERNATIONAL SYMPOSIUM

FIELD SCREENING METHODS FOR HAZARDOUS WASTE SITE INVESTIGATIONS

October 11-13, 1988

Co-Sponsors
U.S. Environmental Protection Agency
U.S. Army Toxic and Hazardous Materials Agency

DISCLAIMER

Although this Proceedings Document reports the oral and poster presentations and discussions that occurred during this Symposium funded by the United States Environmental Protection Agency, the contents represent views independent of Agency Policy. This Document has not been subjected to the Agency's peer review process and does not necessarily reflect the Agency views. No official endorsement should be inferred.

SYMPOSIUM ORGANIZATION

Symposium Chairman – Llewellyn Williams, EPA/EMSL-Las Vegas, NV
Vice-Chairman – Vernon Laurie, EPA/OADEMQA-Washington, D.C.
Vice-Chairman – John Koutsandreas, EPA/OADEMQA-Washington, D.C.
Exhibit Chairman – Joseph Roesler, EPA/EMSL-Cincinnati, OH
Poster Session Chairman – Donald Gurka, EPA/EMSL-Las Vegas, NV

ACKNOWLEDGMENTS

This symposium has been arranged through an Environmental Protection Agency contract with ICAIR, Life Systems, Inc. (as a subcontractor to Acurex Corp.) Mr. Gregory Schiefer and Ms. Jo Ann Duchene managed the Project. Mr. Charles Tanner served as Exhibit Coordinator; Mr. Jack Lanigan coordinated the oral and poster presentations.

FOREWORD

This International Symposium was initiated to respond to the need for a specialized forum to address hazardous waste site investigations and the opportunities afforded by new and emerging technologies to reduce costs, reduce turnaround time of data and increase the scientific confidence in decisions based upon site investigation data.

The objective of this meeting was to bring an international view to problems of hazardous waste site characterization and monitoring.

- To discuss available and developing technology for rapid, low-cost detection and monitoring of toxicants on site.
- To address new opportunities for Federal/private cooperative ventures to develop and commercialize field monitoring technology.
- To inform Symposium delegates and scientists through open discussions, technical sessions, exhibits and peer-reviewed publications of new approaches to solve site investigation problems.

The papers and discussions that follow represent three days of intense communication and cooperation among a variety of communities – regulatory, academic, industrial and user. It is my hope that the products of this symposium will find many widespread uses and will provide the impetus for new initiatives in field screening methods.

Llewellyn R. Williams
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada

CONTENTS

SESSION 1:
Opening Plenary Session

Introductory Remarks – Llewellyn Williams, Environmental Monitoring Systems Laboratory, Las Vegas 1

Welcoming Address – Robert Snelling, Acting Director, EPA, Environmental Monitoring Systems Laboratory, Las Vegas 1

Keynote Address – John Skinner, EPA, Director, Office of Environmental Engineering and Technology 3

Field Monitoring Methods and Use for Superfund Analyses, I – Joan Fisk, EPA, Office of Emergency and Remedial Response 7

Field Monitoring Methods and Use for Superfund Analyses, II – Carla Dempsey, EPA, Office of Emergency and Remedial Response 11

Field Monitoring Methods and Use for Superfund Analyses, III – Scott Fredericks, EPA, Office of Emergency and Remedial Response .. 15

Screening Environmental Pollutants and Biomarkers: The Analytical Challenge – Tuan Vo-Dinh, Oak Ridge National Laboratory 17

SESSION 2:
Fiber Optics and Chemical Sensors (I)
Chairman: Larry Eccles – EPA, Las Vegas

Monitoring of Gasoline Vapor and Liquid by Fiber Optic Chemical Sensor (FOCS) Technology
S.M. Klainer, K. Goswami, D. LeGoullon, D.K. Dandge, ST&E, Inc.; J.R. Thomas, Fiber Chem, Inc.; S.J. Simon, Lockheed-EMSCO; L. Eccles, EPA 25

The Suitability of Surface Enhanced Raman Spectroscopy (SERS) to Fiber Optic Chemical Sensing of Aromatic Hydrocarbon Contamination in Groundwater
M.M. Carrabba, R.B. Edmonds, P.J. Marren and R.D. Rauh, EIC Laboratories, Inc. 31

Fiber-Optic Surface-Enhanced Raman System for Field Screening of Hazardous Compounds
T.L. Ferrell, E.T. Arakawa, R.B. Gammage, D.R. James, J.P. Goudonnet, R.C. Reddick, J.W. Haas and E.A. Wachter Health and Safety Research Division, Oak Ridge National Laboratory 41

Porous Fiber Optic for Chemical Sensors
M.R. Shahriari, Q. Zhou and G.H. Sigel, Jr., Rutgers University and G.H. Stokes, GEO-Centers, Inc. 43

Improved Luminescence Technique for Screening Aromatic Contaminants in Environmental Samples
R.B. Gammage, J.W. Haas III, G. H. Miller and T. Vo-Dinh, Oak Ridge National Laboratory 51

Detection of Solvent Vapors Using Piezoelectric Sensors
E.B. Overton, D. A. Gustowski, L.H. Grande, H.P. Dharmasena, P. Klinkhachorn, C.S. Milan, and G.R. Newkome, Louisiana State University 57

SESSION 3:
X-Ray Fluorescence Spectrometers
Chairman: *Harold Vincent – EPA, Las Vegas*

Introduction by Harold Vincent 61

Application of Field-Portable XRF to Hazardous Waste Characterization
R.K. Glanzman, CH2M Hill 63

The Use of Transportable X-Ray Fluorescence Spectrometer for On-Site Analysis of Mercury in Soils
D.J. Grupp, D.A. Everitt, R.J. Bath, NUS Corporation; R. Spear, USEPA Region II 71

The Determination of Minimum Detection Limits for Inorganic Constituents in Soil Using Transportable Secondary Target X-Ray Fluorescence. I. Arsenic in the Presence of Lead
D.A. Everitt, D. Grupp, R.J. Bath, NUS Corporation; R. Spear, USEPA Region II 73

The Application of X-Ray Fluorescence Technology in the Creation of Site Comparison Samples and in the Design of Hazardous Waste Treatability Studies
J.J. Barich, III, EPA Environmental Services Division, Seattle, WA; R.R. Jones, EPA Quality Assurance Management Office, Seattle, WA; G.A. Raab, Lockheed Engineering Management Services Co.; J.R. Pasmore, Columbia Scientific Industries Corporation 75

Low Level XRF Screening Analysis of Hazardous Waste Sites
R. Perlis and M. Chapin, Ecology and Environment, Inc. 81

SESSION 4:
Fiber Optics and Chemical Sensors (II)
Chairman: *Larry Eccles – EPA, Las Vegas*

Wavelength Tunable Portable Laser for Remote Fluorescence Analysis
G.D. Gillispie and R. St. Germain, North Dakota State University 95

Field Screening for Aromatic Organics Using Laser-Induced Fluorescence and Fiber Optics
W. Chudyk, K. Pohlig, N. Rico, and G. Johnson, Tufts University 99

Second-Derivative Ultraviolet Absorption Monitoring of Aromatic Contaminants in Groundwaters
J.W. Haas III, E.Y. Lee, C.L. Thomas and R.B. Gammage, Oak Ridge National Laboratory 105

Hazardous Waste Analysis by Raman Spectroscopy
C.K. Mann and T.J. Vickers, Florida State University 111

Prototype Design and Testing of Two Fiber-Optic Spectrochemical Emission Sensors
K.B. Olsen, J.W. Griffin, D.A. Nelson and B.S. Matson, Pacific Northwest Laboratory;
P.A. Eschbach, Washington State University 117

Porous Glass Fiber Optic Sensors for Field Screening of Hazardous Waste Sites
S.M. Finger, P.B. Macedo, A.A. Barkatt, H. Hojaji, N. Laberge, R. Mohr, M. Penafiel, Catholic University of America 127

Instrumentation and Methodology for Multicomponent Analysis Using In Situ Laser-Induced Fluorescence
J.E. Kenny, G.B. Jarvis and H. Xu, Tufts University 133

SESSION 5:
Soil Gas Analyzers
Chairman: *Philip Durgin – EPA, Las Vegas*

Influence of Naturally Occurring Volatile Compounds on Soil Gas Results
R.J. Nadeau, EPA, Environmental Response Team, Edison, NJ; J. Tomaszewicz, ERT Technical Assistance Team 141

An In-Situ Technique for Measuring Soil-Gas Diffusivity
P.M. Kearl, T.A. Cronk and N.E. Korte, Oak Ridge National Laboratory 149

A Field Method for Determination of Volatile Organics in Soil Samples
T.M. Spittler, M.J. Cuzzupe, EPA Region I; J.T. Griffith,Goldberg, Zoino and Assoc. Inc. 155

Soil-Gas Sampling at a Site with Deep Contamination by Fuels
H.B. Kerfoot, S.R. Schroedl, Lockheed Engineering and Sciences Co. and J.J. D'Lugosz, USEPA, EMSL-LV 159

Soil Gas Analyses to Delineate a Plume of Volatile Organic Compounds from a Hazardous Waste Site in Williamson County, Tennessee
R.W. Lee, USGS, Nashville, TN; M. Fernandez, USGS, Tampa, FL 171

Soil-Gas Screening: Its Theory and Applications to Hazardous Waste Site Investigations
L.M. Preslo, R. Pavlick and W.M. Leis, Roy F. Weston, Inc. 179

SESSION 6:
Air Sampling Methods
Chairman: *William McClenny – EPA, RTP*

Atmospheric Analysis by Open Path Infrared Spectroscopy
P.L. Hanst, Infrared Analysis, Inc. 181

Development of the MINITMASS, a Mobile Tandem Mass Spectrometer for Monitoring Vapors and Particulate Matter in Air
H.L.C. Meuzelaar, W.H. McClennen, N.S. Arnold, T.K. Reynolds, W. Maswadeh, P.R, Jones and D.T. Urban,
Center for Micro-Analysis and Reaction Chemistry, University of Utah 195

The Preparation, Certification, and Use of Summa Canister External Performance Evaluation Samples in Support of the TAGA 6000E Indoor Air Analyses During the Love Canal Emergency Declaration Area Habitability Study
K.J. Caviston, R.E. Means, R.M. Harrell, B.J. Carpenter, Northrop Services, Inc.;
D. Mickunas and M. Bernick, Roy F. Weston, Inc.; T.H. Pritchett, USEPA Environmental Response Team 205

Unambiguous Identification and Rapid Quantitation in Field Air Monitoring Using a Fully Mobile Mass Spectrometer
F.H. Laukien and T.M. Trainor, Bruker Instruments, Inc. 207

The Preparation of Summa Canister Performance Samples and their Subsequent Analysis by the TAGA 6000E MS/MS
R.M. Harrell, R.E. Means, K.J. Caviston, NSI Technology Services Corp.; M. Bernick, D. Mickunas,
Roy F. Weston, Inc., T.H. Pritchett, USEPA Environmental Response Team; W.J. Mitchell, USEPA Environmental
Monitoring Systems Laboratory, Research Triangle Park. 219

Results From the Environmental Response Team's Preliminary Evaluation of a Direct Air Sampling Mass Spectrometer
R.E. Hague, Rutgers University; K. Cho, Roy F. Weston, Inc.; T.H. Pritchett,
USEPA Environmental Response Team; B. Shapiro, formerly of Enviresponse, Inc. 227

SESSION 7:
Immunochemical Methods
Chairman: *Jeanette Van Emon – EPA, Las Vegas*

Introduction by Jeanette Van Emon 233

Delivery System for Rapid, Semi-Quantitative Analysis of Low Molecular Weight Contaminants and Residues
P.L. McMahon, R. Suva and C. Brooks, IDEXX Corp. 235

Fieldable Enzyme Immunoassay Kits for Pesticides
P.H. Duquette, P.E. Guire, and M.J. Swanson, Bio-Metric Systems, Inc. 239

Integrated Immunochemical Systems for Environmental Monitoring
J.M. Bolts, S.E. Diamond, J.F. Kolc, S.H. Lin, F.J. Regina, Allied-Signal Corporate Technology; P.G. Koga, G.C. Misener and J.C. Schmidt, Bendix Environmental Systems Division. 243

Immunochemical Quantification of Dioxins in Industrial Chemicals and Soils
M. Vanderlaan, B. Watkins, and L. Stanker, Lawrence Livermore National Laboratory 249

Remote, Continuous, Multichannel Biochemical Sensors Based on Fluoroimmunoassay Technologies
J-N. Lin, P. Kopeckova,* J. Ives, H. Chuang, J. Kopecek,* J. Herron, H-R. Yen, D. Christensen, J.D. Andrade, University of Utah; *Institute for Macromolecular Chemistry, Prague, Czechoslovakia 251

A Microbial Bioassay Developed for Rapid Field Screening of Hazardous Waste Sites
I.C. Felkner, B. Worthy, T. Christison, and C.F. Chaisson, Technical Assessment Systems, Inc. 253

SESSION 8:
Portable Gas Chromatographs
Chairman: *Steve Billets – EPA, Las Vegas*

Monitoring Volatile Organics in Water by a Photovac Portable Gas Chromatograph With Multiple Headspace Extraction Method
J.S. Ho and J.F. Roesler, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, OH; P. Hodakievic, Technology Applications, Inc. 261

Hazardous Waste Site Measurements of PPB Levels of Chlorinated Hydrocarbons Using a Portable Gas Chromatograph
A. Linenberg, Sentex Sensing Technology, Inc. 271

Correlation Chromatography with a Portable Microchip Gas Chromatograph
E.B. Overton, R.W. Sherman, C.F. Steele, and H.P. Dharmasena, Institute for Environmental Studies, Louisiana State University 275

Development of a Field Portable Concentrator/Purge and Trap Device for Analysis of Volatile Organic Compounds in Ambient Air and Water Samples
R.W. Sherman, E.S. Collard, M.F. Solecki, T.H. McKinney, L.H. Grande and E.B. Overton, Institute for Environmental Studies, Louisiana State University 279

Ambient Air Sampling With a Portable Gas Chromatograph
R.E. Berkley, USEPA, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 283

A Portable System Under Development for the Detection of Hazardous Materials in Water
J.C. Schmidt, P.G. Koga, G.C. Misener, Environmental Technologies Group, Inc. 291

SESSION 9:
Expert Systems for Field Instrumentation
Chairman: *Joseph Roesler – Cincinnati Engineers, Inc.*

Design and Performance of a Mobile Mass Spectrometer Developed for Environmental Field Investigations
T.M. Trainor and F.H. Laukien, Bruker Instruments, Inc. 299

Expert Systems to Assist in Evaluation of Measurement Data
D.G. Greathouse, Risk Reduction Engineering Laboratory, USEPA, Cincinnati, OH 311

A Positioning and Data Logging System for Surface Geophysical Surveys
J.E. Nyquist and M.S. Blair, Oak Ridge National Laboratory 315

Prototype Volatile Organic Compound (VOC) Monitor
J.D. Wander, Air Force Engineering and Services Center, Tyndall AFB, B.L. Lentz, L. Michalec, and V. Taylor, S-CUBED, Corporation 319

Environmental Field Sampling Expert System Development of a Soil Sampling Advisor
R.A. Olivero, R.E. Cameron, K.J. Cabble, M.T. Homsher, M.A. Stapanian, Lockheed Engineering & Services Company; K.W. Brown, USEPA, Las Vegas, NV 325

SESSION 10:
Other Advanced Field Techniques
Chairman: ***Ronald Mitchum – EPA, Las Vegas***

Introduction by Ronald Mitchum 341

Evaluation of a Field-Based, Mobile, Gas Chromatograph-Mass Spectrometer for the Identification and Quantification of Volatile Organic Compounds on EPA's Hazardous Substances List
A. Robbat, Jr. and G. Xyrafas, Tufts University 343

Ion Mobility Spectrometry for Identification and Detection of Hazardous Chemicals
J. Reategui, T. Bacon, G. Spangler, J. Roehl, Environmental Technologies Group, Inc. 349

Utilization of Short-Term Bioassessments and Biomonitoring at Superfund Sites
D.W. Charters, USEPA, Edison, NJ 359

High-Performance Liquid Chromatograph as a Viable Field Screening Method for Hazardous Waste Site Investigations
V. Ekambaram and J.B. Burch, Woodward-Clyde Consultants 361

Specific Detection of Any Gas Chromatographable Element in Sediment Extracts
M. Szelewski and M. Wilson, Hewlett-Packard Company 367

The U.S. EPA Field Analytical Screening Project (FASP)
G.H. Chapman, Ecology and Environment Inc. and S. Fredericks, USEPA Hazardous Site Evaluation Division 375

CLOSING PLENARY SESSION

Concluding Remarks, Llewellyn Williams, Symposium Chairman 379

POSTER PRESENTATIONS

Quality Assurance Plan Used at the Love Canal Emergency Declaration Area Indoor Air Analyses by the TAGA 6000E Mass Spectrometer/Mass Spectrometer
T.H. Pritchett, USEPA Environmental Response Team; D.B. Mickunas and N. Kurlick, International Technology, Inc. 381

The Kwik-Skrene Analytical Testing System: Description of a Tool for Remediation of PCB Spills
G.R. Woollerton, S. Valin and J.P. Gibeault, Syprotec, Inc. 387

A New Method for the Detection and Measurement of Aromatic Compounds in Water
J.D. Hanby, Hanby Analytical Laboratories, Inc. 389

Development of a Temperature Programmed Microchip, High Resolution GC/MS for VOC Analysis
E.B. Overton, E.S. Collard, H.P. Dharmasena, P. Klinkhachorn, and C.F. Steele, Institute for Environmental Studies, Louisiana State University 395

Applications of the Pyran Thermal Extractor-GC/MS for the Rapid Characterization and Monitoring of Hazardous Waste Sites
C.B. Henry, E.B. Overton, Institute for Environmental Studies, Louisiana State University; C. Sutton, Ruska Instruments 399

Field Deployable Instrument for the Analysis of Semivolatile Organic Compounds
E.B. Overton, C.B. Henry, Institute for Environmental Studies, Louisiana State University, C. Sutton, Ruska Instruments 407

Evaluation of Microwave Detection Techniques to Prepare Solid and Hazardous Waste Samples for Elemental Analysis
P.M. Grohse, D.A. Binstock, and A. Gaskill, Jr., Research Triangle Institute; H.M. Kingston, National Bureau of Standards and C. Sellers, USEPA Office of Solid Waste 411

Rapid Screening of Organic Contaminants Using a Mobile Mass Spectrometer in the Field
M.C. Hadka, Walter B. Satterthwaite Associates, R.K. Dickinson, United Engineers 423

Determination of Chlordane in Soil by Enzyme Immunoassay
R.J. Bushway, J. King and B. Perkins, University of Maine; W.M. Pask, Purdue University; B.S. Ferguson, ImmunoSystems, Inc. 433

Development of a Protocol for the Assessment of Gas Chromatographic Field Screening Methods
M.T. Homsher, V.A. Ecker, M.H. Bartling, L.D. Woods and R.A. Olivero, Lockheed Engineering and Sciences Co.; D.W. Bottrell and J.D. Petty, USEPA, Las Vegas NV 439

Cost Analysis for Using Mobile Laboratories vs. Fixed-Base Laboratories for Site Characterization at FUSRAP Sites
G. Ganapathi and D.S. Adler, Bechtel National, Inc.; M. Carkhuff, Weston Analytical Laboratory 463

Enzyme Immunoassay for the Quantitation of an Alkaline Protease in Airborne Samples
L.S. Miller, V. Moore, A. Wardwell, M. Buchwalter, L.A. Smith, Battelle Biotechnology Section 469

Gas Chromatographic and Mass Spectrometric Analysis of Target Air Toxics at Remedial Hazardous Waste Sites
D.W. Hodgson, B.G. Miller, R.A. Ross and T.S. Viswanathan, NSI Technology Services Corp.; R.D. Kleopfer and W.W. Bunn, USEPA, Kansas City, KS 475

On-Site Soil Gas Analysis of Gasoline Components Using a Field-Designed Gas Chromatograph-Mass Spectrometer
A. Robbat, Jr. and G. Xyrafas, Tufts University 481

Reflectance Spectroscopy (0.2 to 20 μm) as an Analytical Method for the Detection of Organics on Soils
T.V.V. King and R.N. Clark, USGS, Denver, CO 485

Field Use of a Microchip Gas Chromatograph
R.W. Sherman, T.H. McKinney, Institute for Environmental Studies, Louisiana State University; M.F. Solecki, National Oceanic & Atmospheric Administration, Seattle, WA; R.B. Gaines, U.S. Coast Guard R&D Center, Groton, CT; B. Shipley, USEPA Region IX 489

Rapid Assessment of PCB Contamination at Field Sites Using a Specialized Sampling, Analysis and Data Review Procedure
W.W. Freeman and J. Karmazyn, Roy F. Weston, Inc. 491

Participants' List 501

INTRODUCTORY REMARKS

LLEWELLYN WILLIAMS

Welcome to The First International Symposium on Field Screening Methods for Hazardous Waste Investigations. I am very excited about this area and about the response that we've had since our initial call for papers last December. We have had dramatic response from people who design, produce, and use new technology for monitoring and for measurement.

The timing for this Symposium is right. We have brought together some of the most outstanding representatives of academia, the private sector, and the federal sector. This program brings together strong presentations from national and international sources. One of its features is the combined reception, exhibit and poster session, which is an opportunity to view some of the new technologies that are available and to discuss your future needs with the designers of those technologies. I've found that the private sector is anxious to respond to the user's needs as long as they are made clear. If you are such a user, be sure to let them know that there is indeed a market for this technology not only in the future, but now.

WELCOMING ADDRESS

ROBERT SNELLING

Welcome to Las Vegas. I think we have an outstanding program for you. My job this morning is two fold. First of all, I'd like to provide a few general words as to why we are here, and to provide an overview of our program here at the Environmental Monitoring Systems Laboratory.

The reality, in terms of hazardous waste site assessments, is that we are in the dark. We are faced with the problem of trying to feel our way through the darkness, to get some insight into the problems associated with a particular hazardous waste site. That is the thrust of this program. With the support and encouragement of the Superfund Office within EPA, a program was initiated two years ago which attempted to identify and establish rapid screening methods that could be applied to hazardous waste site investigations.

What do we mean by screening methods? In academic terms, it is the use of rapid, low-cost test methods to determine whether a characteristic of interest is present or absent, above or below a predetermined threshold at a given site, or in a concentration within a predetermined range of interest. It is an attempt to define the spatial extent of some specific characteristic.

We are interested in examining various screening methods because we wish to gain a preliminary understanding of what happens at a hazardous waste site. This can, in turn, guide us toward a cost effective monitoring program, which is essential, since monitoring, sampling and analysis are currently very expensive. So the emphasis of the program will be on aspects of field measurements, quick turn around, and low-cost screening methods.

There are four primary aspects to the program which we have defined in order to achieve these goals. The first is identification of off-the-shelf technology, which is either already available on the commercial market, or is at a stage in its development where it can be made available shortly. Technologies are available that are not used, or not fully characterized. We must develop a sense of the validity and applications of a given method.

The second part of the program is to identify the needs in the field which are being met by existing technology. In response to these findings, a research and development program was initiated to fill those needs. This program evaluates technologies that are not quite ready for commercialization, but need some additional research and development.

The third part of the program involves the demonstration of both the commercially available technologies, and the technologies coming out of the methods development program. This provides confirmation that the technologies perform as they are intended to on hazardous waste sites.

The last aspect of the program is to transfer this technology to the people who require it. We have struggled with this problem in the EPA, because we have found that the knowledge gained in the research and development community has not been communicated to the regional, state and private sectors who are engaged in the work itself. An important part of the program is to transfer this technology to the people who need to use it. That, in part, is why we are here.

The overall program strategy has a number of interesting components; I would like to emphasize one in particular, which involves three aspects of the program: the leverage of the private sector, technology and matrix management within the Agency. We felt that the evolving technologies required a mix of expertise. So our program utilizes a number of our research laboratories through a matrix management program. We have tried to incorporate the needs and inputs of the EPA Regional offices, who are our primary clients. We are also very interested in leveraging other agencies, where a lot of work is being done. For example, the Department of Defense is working on field measurement techniques, which can, in part, be transferred to the environmental programs.

The aspect of the program we really want to emphasize, however, is leveraging of the private sector, with special emphasis on those technologies which are either currently commercialized or will shortly be ready for commercialization. This topic will be discussed in part, during the next speaker's talk on The Superfund Innovative Technology Evaluation Program, in which we will work with the private sector to evaluate technologies that might be applied to hazardous waste site investigations.

Other aspects of our program attempt to focus on this specific issue. We have found that a great deal of work is being done in other programs, and we have tried to pull these together across EPA's media programs, to focus on the technologies themselves.

There is a need in the field to gather information quickly and cost effectively, rather than using old, time-consuming methods such as collecting samples, sending them to a laboratory, and then waiting three weeks to receive an analysis at the cost of thousands of dollars. We need methodologies that will give us preliminary insight while we are still in the field, which we can subsequently act on. Those are the kinds of technologies that we want to focus on in the coming days.

KEYNOTE ADDRESS

Dr. John Skinner
Director
Office of Environmental Engineering and Technology
U.S. Environmental Protection Agency

I am going to discuss the program evaluating and demonstrating field monitoring methods for hazardous waste sites and the use of the Superfund Innovative Technology Evaluation program or the SITE program for this purpose.

This field is very important to EPA for a number of reasons. We and the private sector spend hundreds of millions of dollars every year evaluating and analyzing samples for various chemical constituents. Any reduction in cost or time consumption which can be achieved in that process should result in enormous savings, both for the Agency and for all of the regulated parties. So it should be obvious why this effort to develop field screening and field monitoring methods is important. There has been a considerable expansion of sampling and monitoring requirements, due to the passage of SARA, the Superfund Authorization Amendments. Many more sites will enter the Superfund program, and much more sampling and analysis will be required both at the early site characterization stage and in judging the validity or acceptability of the clean-up.

However, the technologies that we will be discussing today are not limited only to the Superfund program. They are applicable also to the hazardous waste regulatory program under RCRA, the Resource Conservation and Recovery Act. These technologies could apply to other Agency programs as well, such as waste water discharges from industrial and municipal sewage plants, or analysis of pesticide residues; these technologies should be useful across the Agency.

As our regulatory programs expand, and as Superfund itself expands to include more sites, the current laboratory capacity will be taxed. Higher cost of sampling and analysis and long delays in getting the results will be the outcome.

It is important to define field screening and field monitoring methods. These are methods that can be taken to the field, to carry out--in a matter of hours or days--screening activities to identify the nature of contamination at that site. These methods may not all be as accurate or precise as the laboratory methods, although some of them are very accurate and precise. But the idea behind them is to allow priorities to be set at a site; to allow identification of hot spots, and to quickly establish either a more comprehensive monitoring program for a given site, or to place the site in some priority order relative to another site. We believe that these field screening methods have the potential to accelerate site clean-up, to improve confidence in site clean-up, and to reduce costs. Let me touch on each one of these.

With respect to accelerating site clean-up, the critical time line elements generally are the requirements for on-site sampling, the shipment of those samples to a laboratory, and the analysis of those samples at the laboratory. Delays can be caused throughout this entire process. So, if a site can be quickly screened to eliminate some of these delays, thereby moving on to more full scale site monitoring sooner, it should be possible to accelerate the site clean-up.

With respect to improving confidence in the clean up, it should be possible to do more sampling at a higher sampling density without excessive costs. This would lead to more effective delineation of contaminants on the site, detection of hot spots or spots that should be cleaned up first or quickly, and identification of which areas might require even more intensive sampling in order to be properly characterized.

In terms of cost reduction, these techniques could reduce or minimize the laboratory analyses thereby minimizing the stand-by time for sampling personnel who await the results of the analysis in order to determine whether more sampling is necessary. If additional sampling is deemed necessary, it can then be done right away. It is also possible to minimize time for clean-up personnel, who may be waiting for confirmatory sampling to determine whether they really have cleaned up the site to the required level. So, reduction of personnel costs, both for sampling and clean-up, should result in overall cost reductions.

The Las Vegas team performed some rough calculations to determine the potential of some of these technologies. They looked first at a metals analysis in soils. They assumed that at a particular site they had to analyze 500 samples for lead, copper, and zinc. For example, if atomic absorption were used in a laboratory to do that, the

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sample turn-around time would be roughly one month. To do those 500 samples would cost roughly $20,000 to $25,000. If the same process were done in the field with X-ray fluorescence, the samples' turn-around time would be less than one day. The results could be found the same day, and the cost would be a few thousand dollars.

Even if these numbers are inaccurate by a factor of two or three, the potential both for reducing the turn-around time and for reducing the costs of sampling are extremely significant. This only pertains to the costs of doing the analysis; it does not even account for the standby cost that I just mentioned.

Similarly, with respect to organics, an analysis was done which demonstrated that if 500 samples of ground water or leachate were analyzed for pentachlorophenol using typical laboratory GC/MS, the sample turn-around time would be 30 days. No laboratory is able to turn around samples for organics in 30 days. The time estimated is at least double or triple that, and the cost is approximately $50,000.

With the use of immunoassay at a site, samples can be turned around in one day with a cost of a few thousand dollars. Thus, both for inorganics and organics, the potential for cost and time reduction with some of these field screening methods is quite substantial.

I would now like to address the process of accelerating the development and application of some of these field screening methods, using the SITE program. This program was established under the Superfund amendments. This is not an area in which the federal government would carry out extensive technology development on its own. Rather, the focus of this effort is to create a market for private sector developments and to form a relationship with the private sector which would encourage the development of those technologies.

The approach will be to establish desirable performance standards for these technologies. Next, an evaluation or a demonstration of those technologies will be carried out at an actual Superfund site. In general, when such a demonstration is performed, the private developer is expected to pay for the actual cost of running a technique at his site. We would pay for the costs of evaluating the technique, then publish those results. Those technologies that were successful would then be used in the Superfund program or in the hazardous waste program, in place of more traditional technologies. Thus, the demonstration program would eventually lead to the potential commercial use of these technologies in the actual Superfund cleanup program.

The primary purpose of the SITE program, which was established under the 1986 amendments to Superfund, is to enhance private sector development of technologies through a demonstration or evaluation process which establishes the commercial availability of these technologies. This is accomplished through a site demonstration which tests and validates these field monitoring methods under one or more real waste site conditions. The performance of these technologies can be confirmed through laboratory sampling and analysis, and the entire demonstration effort can be coordinated with the potential users of these technologies. Our Regional offices, the REM/FIT contractors, who carry out actual Superfund cleanups, would document the performance of the technologies and put out a report.

We will select these technologies in a number of ways, both formally and informally. Formally, this program has been announced a number of times in the Commerce Business Daily. We have received a fair response from the private sector to our interest in evaluating these technologies.

Informally, we follow up on good ideas when they present themselves to us. We actively pursue information about these technologies. If anyone here is a developer or knows someone who is, please contact the individuals listed on the sheets which were distributed to you today. We believe that a large number of technologies will be eligible for the program. Federal support is not as limited for the development of the technology as it is for testing and evaluation.

Examples of the types of technologies in which we are interested, some of them already in the program, are generally portable, transportable, and fieldable instruments. These include portable GC/MS of suitcase size, portable X-ray fluorescence systems, chemical and immunochemical field kits, technologies to detect in situ contaminants in soil, soil gas, ground water, and other innovative sampling and collection methods.

Before going ahead with a demonstration we would like the following information. The developer should define, from whatever data he has, the bias, precision, the rate of false positive and negatives, the detection limits, and the major interferences of an instrument. Further, he should define analytes and the matrices to which he thinks the technology is applicable; provide his set of standard operating procedures and protocols; and provide whatever data he has from his independent evaluation of the technology.

A demonstration plan would then be devised in cooperation with the developer. This would vary according to the technology, defining the role of the developer, and our own role in the demonstration program. Quality assurance would be emphasized in the demonstration plan so that good data would be produced. In the process, we would arrange for active participation of our Regional offices, our contractors, and our private sector representatives.

We want to ensure that these technologies ultimately suit the needs of our clients, who will use them after the demonstration projects have been completed. The performance of these technologies must be confirmed through the contract laboratory program.

The products are expected to be a fair and objective evaluation of the technology in a "real-world" field situation. A demonstration report would be issued, which includes the data that have been collected, and discusses the strengths, limitations, and potential applications for the program. This effort creates a number of opportunities for EPA to work with the private sector, in the type of relationship that we think works very well.

The government is not in the business of commercializing technologies. We feel that there are very significant private, profit incentives, for doing just that. We are trying to create the framework in which private sector development can proceed, and we feel that this is a genuine partnership. We have a mutual interest with private developers in getting better technologies and bringing them to the marketplace. We hope that this will open up some new markets, both within the Superfund program and outside of it for other programs in the Agency. We believe there are mutual benefits, both to the developer and to the potential user of the technology. This is one area in which both the regulator and the regulated party should benefit.

In conclusion, I wish you all success for a very productive and informative conference, this First International Symposium on Field Screening Methods. I think the papers that will be presented over the next three days offer some very exciting new opportunities for improved field screening techniques. We hope that these efforts will eventually pay off in reducing the delays in sampling and analysis of chemicals at Superfund sites and will also result in the creation of new markets for some of these technologies.

FIELD MONITORING METHODS AND USE

FOR SUPERFUND ANALYSES, I

Joan Fisk
Organics Section Chief
Office of Emergency and Remedial Response
U.S. Environmental Protection Agency

I will begin with an overview of the work of Superfund and its contractors in the past and present. Carla Dempsey will then discuss the QA aspects and guidance for appropriate use. Finally, Scott Fredericks will follow up with our success story on field methods that have worked well because of the procedures they have set up.

I am going to give some background to explain why Superfund is seeking out the use of field methods extensively. Superfund, The Comprehensive Environmental Response, Compensation and Liability Act was enacted by Congress in 1980. It gives the President of the United States the authority to clean up uncontrolled hazardous waste sites that are a threat to public health or the environment. A total of $1.6 billion was raised by Superfund from taxes on chemicals and chemical companies to effect this clean up. In addition, EPA was permitted to recover costs from any potentially responsible parties that could be identified.

Superfund was reauthorized as the Superfund Amendments and Reauthorization Act in October 1986, with changes and additions. Today, however, I will only be discussing those changes in schedules which set time limits for programs during the life of Superfund. First of all, a list called the Comprehensive Environmental Response and Liability Information System (CERCLIS) was created, citing 28,000 potential sites which existed at the time of Superfund's reauthorization. A deadline of January 1 was set, at which time these Preliminary Assessments all had to be completed. The EPA met that deadline, leaving a backlog of about 10,000 Site Investigations which were also supposed to be completed at that time.

The next item on the schedule demanded evaluation of all sites on the CERCLIS within four years, upon the recommendation of the Preliminary Assessment and Site Investigations. In other words, the scoring process called the hazardous ranking system (HRS) must be employed at each site to determine whether or not it gets placed on the National Priorities List (NPL). I believe that right now 797 sites are on the NPL and 380 are proposed. This is a dynamic number which changes as sites are cleaned up or discovered.

The next step in the Superfund dynamics is the Remedial Investigation/Feasibility Study (RI/FS), done on all sites which are on the NPL in order to determine the extent of contamination. That is, the concentrations and the boundaries of pollutants at a site, whether groundwater, air, soil, and so on are determined. No less than 275 RI/FS's were supposed to be completed by October, 1989. By the end of Superfund, a total of 750 are to be completed.

In addition to identification of the extent of contamination, the selection of remedy options is also carried out during this period of time. Ultimately a decision emerges, which takes socioeconomic factors into consideration. These factors include proximity of the site to other areas, resources available for doing the job, and health risk assessment.

The last step of the Superfund process is the most important: the design for remedial action at a given site. One hundred and seventy-five of these must be done by October 1989, and a total of 375 by the end of the existing Superfund law. Winston Porter, in August of 1987, sent out a letter to Regional Administrators suggesting they speed up the remediation process, and complete a RI/FS in 18 months or less. Clearly, there is a big push to use faster field methods.

All of this activity will result in an enormous quantity of samples for analysis by some technique or other. Traditionally, most Superfund analyses were given to the Contract Laboratory Program (CLP), which has about 100 contractor laboratories nationwide performing analyses using standardized protocols with standardized deliverables. Many quality control (QC) requirements and criteria must be met and there is a great deal of documentation on the QC, so that the data are of a known quality.

This much care was taken because it was assumed in the early days of Superfund that all data could undergo the scrutiny of a court of law, either in a settlement or in litigation. Later, it occurred to some participants that such measures were not necessary, and that alternatives were available.

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During this period, the concept of data quality objectives emerged within the agency. These are qualitative and quantitative statements made by decision makers regarding the required level of certainty acceptable in results of environmental data collection. All of the decision makers throughout the Superfund process are engaged in up-front planning to determine the type of data they will need through each one of these activities. The decisions made are the key to when and how field screening can be appropriately used. In 1985 Superfund did make a commitment to connect decision-making and data quality needs, through a letter from Henry Longest.

In summary, the first two items, the schedules and the directive, both show a desire to increase the speed of activity. The last item, the data quality objectives, suggests a need for more ingenuity. Many people are interested in doing work in the field.

These suggestions create a very basic, simple definition of field technologies. "Portable" equipment should weigh 50 or 60 pounds, so it can be carried with minimal sample processing. "Fieldable" equipment is transportable in a van or small truck and requires no more than a portable generator for power. "Mobile" equipment is small enough for a mobile lab or temporary trailer or hut, with a generator and compressed gas cylinder, which actually includes almost anything that can be used in a fixed laboratory.

Discussions with people in the field have yielded three major roles for using field methods of analysis. The first is to enable "real time," on-site feedback, to aid in site characterization by identifying hot spots and the extent of contamination. The use of the word "aid" points up the fact that this technique does not accomplish the task alone. It also aims to direct ongoing work such as redirecting sampling efforts, modifying work plans, determining the depth of well screen placement or making sure all contaminated materials have been removed while the equipment is on the site, so that the costly step of bringing it back a second time is avoided. Field methods can also prioritize samples through the CLP, which is very useful. The majority of people tell us that they do confirm the CLP analysis on about 10% to 30% of all samples. Finally, field methods can assure confidence in a clean up.

The second general reason for using field methods is customized analysis. This is a site-specific approach, which becomes increasingly important during the later stages of the Superfund clean-up process. Customized analyses can optimize methods for dealing with the contaminants in question. These can include the use of specific detectors, screening, grab air samples, or soil gas sampling for samples that have short holding times. We all recognize that the sample that is analyzed in the laboratory is not necessarily representative of the one that was taken out in the field.

The last general reason for using field methods is cost reduction. This is accomplished by minimizing full CLP analyses; or more exactly, by making more effective use of the resources to direct more of the really contaminated samples through the CLP labs thereby eliminating a lot of negatives. Field methods can also minimize stand-by time for sampling crews and clean-up personnel, since the data they are waiting for now takes weeks to generate and deliver.

There are many key organizations involved in this process (Table I). These include EPA's Office of Emergency and Remedial Response and the Hazardous Site Control Division which are, among others, responsible for the REM contractors; the United States Army Toxic and Hazardous Materials Agency (USATHAMA), which works with Oak Ridge National Laboratories; and EMSL Las Vegas, which is part of EPA's Office of Research and Development. The Hazardous Site Control Division does extensive field work using what they call close support laboratories (CSLs).

Table I Key Players in Field Methods Analyses

- EPA, Office of Emergency and Remedial Response (OERR), Site Assessment Branch (SAB) of the Hazardous Site Evaluation Division (HSED) and their Field Investigation Teams (FIT)
- EPA, OERR, Hazardous Site Control Division (HSCD) and their Remedial Investigation/Feasibility Study (RI/FS) contractors (REM)
- EPA, Environmental Response Team (ERT)
- U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) and Oak Ridge National Laboratories (ORNL)
- EPA, Office of Research and Development (ORD)
- EPA, OERR, HSED, Analytical Operations Branch (AOB)

Most of the people I have talked to in the REM contractor community say that they firmly endorse the use of data quality objectives to determine the appropriate use of methods and the appropriate methods themselves. Their process goes as follows. First, they determine the list of indicated parameters from previous data. Next, they establish detection limits, precision and accuracy requirements. Then, they determine the required data completeness or the data deliverables, select or develop a method that meets the above determined data quality objectives, and validate that method, providing performance information on it. They then prepare a standard operating procedure describing the close support lab operating structure, the sample handling, tracking, and the methods, the QA/QC requirements, the data reporting requirements, and health and safety requirements. Last, they include this SOP in the quality assurance project plan for review and approval.

The REM contractors use field screening techniques for the purpose of supporting treatability studies, and supplementing health and safety decision making. This includes levels of protection to be worn out in the field; the type of equipment to be used to monitor the problems in the field; and supplementation of the data base, that is, generating additional analytical data for sites, allowing for more flexible and cost effective use of the CLP laboratories.

As an example, let me relate an actual event that occurred in a trailer park in Region I. In this park, the families had been moved to a hotel, at the government's expense. Clearly this was not a desirable, indefinite arrangement, so extensive work was done right in the field to identify the problems and clean up the park so the occupants could be moved back in.

The Environmental Response Team (ERT) uses soil gas analysis to determine emission sources and/or determine the extent of contamination for underground plumes. They also conduct on-site soil gas analysis training seminars. They use bio-assay analyses and they also teach the Regions the use of bio-assays at hazardous waste sites.

Many people think it quite remarkable that they use a Sciex TAGA(*) 6,000 MS/MS for air sampling and analyses, which is a half-million dollar piece of equipment. However, they do obtain real-time information at very low sensitivities, although they are not particularly suitable for mixtures. The ERT uses these samples to identify plumes, and they send them back to the laboratory for confirmation. They also use atomic absorption, plasma emission, HPLC, GC/MS, and possibly X-ray fluorescence.

The ERT is also well known for its evaluation of commercially available technologies, such as the Brooker MM1 Mobile Mass Spectrometer, remote optical sensing by FTIR; Summa(*) canisters for air sampling; Tenax(*)/carbonized molecular sieve absorbent tubes; the TAGA and various portable GCs.

USATHAMA is providing chemical support to the Rocky Mountain Arsenal, whose program manager was charged with the responsibility of restoring the Arsenal. The clean-up effort is directed toward remedial excavation of areas that are contaminated with specific toxic or hazardous compounds at a defined concentration. USATHAMA has asked Oak Ridge National Laboratory, operated by Martin Marietta Energy Systems for the Department of Energy, to author a document assessing various technologies available for work in the field in order to determine their applicability in characterizing the Rocky Mountain samples. At this point in time, I do not know whether anything but the written assessment is available, or whether there has been any testing of these various methods in the field.

The document which was produced contains many recommendations, including the use of purge and trap with a portable GC/PID detector for volatile samples; the use of heated head space solvent microextraction or solid sorbent for semivolatiles for less sensitive needs; testing of the Cole-Parmer Mixxor(*) for water sample preparation (which is for extraction and concentration and supposedly uses very little solvent and has sufficient recoveries) and use of a Soxtet(*) device which extracts and concentrates in less than 20 minutes with sufficient recoveries and using minimal amounts of solvent. There are also many inorganic recommendations in this document.

The Advanced Field Monitoring Methods (AFMM) program seeks to identify, adapt, and field-demonstrate field monitoring methods, and to facilitate transfer and exchange of information. There are two main components of the program. First, basic research utilizes the competitive process to seek out all of the new technologies mentioned previously: they should be fieldable, portable, qualitative, quantitative, sensitive to the compounds of interests, rapid, and inexpensive. Second, applied research utilizes readily available technologies like X-ray fluorescence, fiber optics, portable GCs, and immunoassays.

My last topic of discussion is the Analytical Operations Branch, which will provide the link between data quality needs and expectations for the generated data quality. It is the focal point for analytical field methods dealing with the EPA Regions, our clients. The organic and inorganic sections will address those technologies which clients hope to have further evaluated or developed, and those compounds for which they wish to use these technologies. As a first step in the process of guidance, the Field Screening Methods Catalogue was published. The catalog presents field screening and analytical techniques being used by the Regions.

In conclusion, Superfund and its contractors are moving forward in a commitment to providing more effective remediation of Superfund sites by utilizing the data quality objective process to match data quality needs with data generated. This action is leading to increased use of field analytical methods which is, in turn, streamlining the process and making more effective use of resources.

(*) Registered trademark.

FIELD MONITORING METHODS AND USE
FOR SUPERFUND ANALYSES, II

Carla Dempsey
Quality Assurance Coordinator
Office of Emergency and Remedial Response
U.S. Environmental Protection Agency

I am going to discuss some current considerations in the field, which arose because of the new uses of field analytical screening methods. Because they have been used only as screening methods for the past eight to ten years, these issues were not problematic up until now. Scott Fredericks will follow my talk by explaining how a field screening analytical methods program can be developed and successfully implemented taking these considerations into account. Such a program has been successfully demonstrated for Superfund.

Many times we gather for group discussions to speak about where a technology is, where we want it to go, how it can be miniaturized, how methods can be forced to lower detection limits. I would like to discuss the use of these methods and to consider their applications as we develop them. I will discuss the current thoughts at Superfund regarding the use, review, and oversight of field screening analytical methods in the program. I use the term analytical/screening because these methods are in actuality used for both screening and analysis.

Field screening analytical methods have been used by Superfund for the past eight to ten years, with support from the REM, TES and FIT contracts, among others. These methods are currently still being used by Superfund. It is indeed appropriate to question why their uses are being examined and doubted after eight to ten years of successful utilization. The answer is that in the past these methods were used primarily for the detection of qualitative differences in chemical concentrations, not to yield "real" numbers for very rigorous decisions. Field teams used the methods to assist them in preliminary health and safety decisions; to locate hot spots or very contaminated areas within sites; and to prioritize samples to send back to the CLP laboratories. Because such decisions were strictly preliminary, there were very few horror stories and many success stories related to the use of these methods.

The SARA schedule for listing deadlines, completing RI/FS's, and so on, has been greatly accelerated. In the recent past, the need to acquire data quickly in order to make site decisions has grown tremendously. Since field screening methods were very successfully used in the rapid acquisition of qualitative data, they were chosen to quicken the acquisition of quantitative data. It is important to note that the acquisition of data does not necessarily determine the role of any site investigation or feasibility study. However, all avenues to reduce the time involved in any part of the Superfund process are now being examined, and all time-saving steps are being utilized.

The transition of the use of field methods from strictly screening tools to analytical tools is occurring right now. This is the reason why we must carefully consider their selection, the QA and QC requirements, the data review requirements, and the use of the resultant data. Because the data are being used to make more demanding decisions, we must be much more careful in our use of the methods.

How can field analytical methods be used? What decisions can be supported by the data? Consider the following statement: Field analytical/screening data are just one type of Superfund analytical data. Just as fixed lab analytical data are one type of Superfund analytical data.

As for any type of Superfund analytical data, the appropriate uses for such data must be defined in order to use them correctly. Furthermore, the definition must be made before the data are acquired, so that the choices of method and the QC requirements can be carefully considered. The review of the data must be also carefully considered. This will indicate what was accomplished in the choice of method, and whether the data which were acquired are usable for the decision they were meant to support. Also, as with any type of Superfund analytical data, the planning and review procedures must be very clearly defined, in order to make correct use of field screening analytical data. The method, QA and QC, and review must be stated in site-specific project plans to assure that appropriate choices have been made. As for any other type of Superfund analytical data, planning must be done and must be documented in the site-specific project plans and other Regional sampling documentation.

The choice of which analytical resource to use is always driven by the requirements of the decision that the data will support. This concept, called the data quality objective (DQO) process, has made it possible for Superfund to use many different

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types of data. Early in the Superfund process, the contract laboratory program and Regional laboratories produced only one type of data, one type of method, one type of very rigorous quality control, one quality assurance program and a very strict review procedure for all data produced for Superfund decision making. Now, we are willing to state the data's uses including the precision requirements and the amount of risk allowable for a false positive or a false negative. This has enabled us to start utilizing alternative methods, alternative QA/QC and alternative review requirements based strictly on the use of that data in the Superfund process.

Now, all types of decisions must be made before data acquisition in order to ensure that the data are suitable. Instead of procuring only one specific type of data for Superfund, we can now use many different types, all appropriately chosen to support our decisions. There are minimum requirements for any kind of Superfund analytical data, no matter what type. These requirements include proper documentation, planning and review as listed in the quality assurance project plans and the site-specific Regional plans in each Region. In addition, appropriate QA and QC must be specified to support the decisions based on the intended use of the data.

There are several reasons for these requirements. Superfund must know the level of quality in any kind of data. The quality of that data must be documented somewhere, so that it can be confirmed at a later date. Because it is documented and planned for, the data can be assessed with regard to its sufficiency and appropriateness for supporting each decision. In addition to these usual requirements for all data, there are some special requirements for field analytical screening methods. Many field analytical methods are very sensitive, because the detection limits are very low. They are outstanding methods. If the object of your search has been identified, it will manifest itself through the use of these methods. We must, in every case, avoid false negatives by identifying that object before choosing a field method which is very specific to one analyte or another. We have some strictly preliminary screening methods to help us in this identification. But if very close characterization of a site is desired, by very rigorous decisions, it is necessary to be certain that the proper tool is being used to detect the chemical which is present at the site. In order to properly choose a fieldable instrument or field method, you must know what you are looking for. The area must be screened with a broad spectrum analysis such as ICAP or GC/MS to look for everything.

The second special requirement is the verification of removal of contaminants by a final broad-spectrum analysis. This means a search for the contaminants of concern. This broad spectrum analysis will occur at an NPL delisting, when remediation has been completed and you need to determine that clean up has occurred down to required protective levels for the site. Many times a field screening tool will be used in the search for indicator chemicals which are easy to track at the site. In many cases, there may not be an examination of all the contaminants that have been found at the site. Therefore, before delisting, there must be a search to confirm that all contaminants of concern at that site have been properly removed. This again will require some kind of a broad spectrum analysis to make sure the site has been cleaned to the protective levels.

The third special requirement is flagging the data for the type of decision it was intended to support. This is necessary because of the existence of such a broad spectrum of field analytical techniques, some of which are truly screening techniques, while others are more analytical tools. It is important that the data are used to support the kind of decision for which it was gathered. In order to appropriately use this data for other decisions, its quality, its method, and the qualitative procedures which were applied to it must be known. In the future, SOPs, performance information and QA/QC requirements for field analytical screening methods will be much better defined. At that point it will be much easier to specify their appropriate use. If we do not have performance information on these methods, it is almost impossible for a manager to effectively choose the right method. So it will be much easier in the future as we gather information, and as our skills improve in the use of these methods, to appropriately choose and utilize them.

In the interim, careful consideration must be given to each proposed use of field screening analytical data. It may work very well at one site with one matrix, but not at another with a different matrix. Until we get very good performance information and until we have standard operating procedures which can be applied from one site to another, each case must be considered.

This does not mean that these methods should not be used, but rather they should be used appropriately. Because of our lack of knowledge, this will be difficult until we have more information.

Many steps are being taken to assist EPA managers in their choices of appropriate methods. For example, a work group at EPA headquarters has been formed to examine the uses of field methods, and the producers of field methods (such as USATHAMA), and to examine the activities of groups such as ERT at Edison. The work group is composed of various users and producers of these methods, and is expanding to include more Regional representation. Out of this group some guidance will be issued on appropriate use of these methods.

Perhaps our most important activity is the development of performance information for these methods based on their use on environmental samples, preferably as demonstrated at Superfund sites.

We are attempting to use available data such as that gathered by the FASP program, and to discuss with users the appropriate functions for such data. We will look at successful uses of the data to support decisions, so that this information can be utilized by other managers within EPA.

We are also updating the catalogue of field screening methods, which serves two purposes. It will furnish more refined performance information, and will serve to transfer the technologies among

Regions. It is our link between the users and the developers of the method. The catalogue will make appropriate choices of field analytical methods much easier. It will provide as much information as possible about the use of these methods, including positive and negative aspects of each: matrix effects, cost, limitations of use, precision and accuracy, quantitative or detection levels, the availability of standards, the availability of SOPs, and QA/QC requirements keyed specifically to the uses of these methods for specific data collection activities.

With broader representation in our work group, we will be able to determine the real need for matrix performance evaluation materials. We suspect, and have been told, that in many cases the standards for real matrix materials are not available, although they are needed in order to actually produce precision and accuracy information for some of these field methods. But in talking to the users from the Regions, we hope to get more information and start production of more performance evaluation materials and standards keyed to this kind of technology.

We will also produce guidance on the appropriate use of this technology. The Regions and the EPA require guidance which will lead managers to appropriately choose this technology rather than repeatedly choosing the CLP's fixed laboratory method. The Field Screening Methods Catalog-User's Guide is EPA publication number 540/2-88/005. It will be transmitted within the next two weeks to the EPA Regions, 50 copies to the Waste Management Division Directors and 50 copies to the Environmental Services Division Directors. A data base accompanies the catalogue, which lists a phone number for further information. We hope to mass produce it very cost-effectively in the near future, but all Regions will have a copy of the data base in the interim.

This manual is a compendium of approximately 31 currently used field methods, including a list of sites where these methods have been used successfully by EPA in the past few years. With every technology, a technical contact is listed who can provide user-support to supplement the limited performance information in the catalogue.

The EPA contractors who would like to receive a copy of the manual should call (513) 569-7562. It is recommended that you specify your position, and give your contract number. The catalogue will then be mailed directly to you. It is also available through NTIS (703) 487-4650, for non-EPA contractors.

In conclusion, proper planning and oversight of the use of field analytical screening methods, as with any new technology, is the key to their successful use now and in the future.

FIELD MONITORING METHODS AND USE FOR SUPERFUND ANALYSES, III

Scott Fredericks
Section Chief
Site Operations and Contracts Section
U.S. Environmental Protection Agency

I work in the Site Assessment Branch at EPA headquarters, which is responsible for the preremedial program. Our Branch performs site inspection and listing inspections to support the listings of sites on the National Priorities List. A field analytical screening program has been developed since the FIT contract is the main tool provided to the Regions for performing site and listing inspections. This is a very large contract, exceeding one million dollars ($1 million) per week. It supports the performance of detailed site inspections on various waste sites by a team of workers in each Region.

When the acronym FASP was first created, it denoted the Field Analytical Screening Program. In retrospect, we realize that it is more appropriately named the Field Analytical Support Program, because it provides a number of different methods and approaches which supplement the CLP's work and benefit the Region as a whole.

Interest in the FASP before 1984 was somewhat sporadic. Field screening methods within our contracts and Regions mostly employed a "sniffer" type of instrumentation to increase safety and to locate hot spots and well screens. Active interest in the program began in 1984, when there was an overload on CLP capacity. With a shortfall of REM contracts (which came on line) and the shortchanging of the preremedial program, we felt there was an inappropriate use of resources. So we began to investigate various methods which could be used for our data needs, and which would be complimentary to the CLP. We commissioned a number of studies during that time which evaluated methods and existing equipment and determined limitations and costs of these methods through communication with manufacturers. I am quite convinced that utilizing the field screening methods of Thomas Spittler, Rick Spear, Tom Yates and others, is a viable approach. The greatest success in the use of FASP has been with the Environmental Services Division Directors and their employees. The Regional people and the contractors, working in tandem, have been responsible for the program's success.

The FASP program began as a national effort, when the FIT contracts were rewarded. The need for a FASP-type of program was actually designed in the proposal and a fixed budget was allocated. We indicated that the use of dedicated FIT teams would be necessary in performing these techniques.

The FASP program was designed to provide flexibility in meeting Region-specific needs. In other words, each Region has a great deal of input regarding the design and operation of its particular FASP program. We envisioned the use of the programs primarily for listing site inspections and for support, where a broad spectrum analysis has already been done, primarily through the CLP. Once we have a fairly clear picture of the compounds involved, we can select an instrument and a method and clearly define our data quality objectives. The FASP can also be used for screening target compounds, for which the data must be matched to data quality objectives.

The benefits of FASP are not perceived but realized benefits: the program does provide quick turnaround of data to aid real-time decisions. It is economical, and also possesses capabilities beyond that of CLP for air monitoring, soil gas sampling and screening. It enables improved site characterization and provides on-site and Regional managers with the immediate information they require to make better decisions and conserve resources. In addition, we perceive the FASP program as a Regional resource above and beyond the preremedial program: it can actually assist in emergency response actions as well as remedial actions.

I would like to give you a short overview of the FASP capabilities in Region X, which, along with Region I, has been our prototype. The FASP program was developed faster in those particular Regions than in others.

In Region X, we have 71% of the CLP's capabilities for volatile compounds; 57% for semivolatile compounds (acids, bases and neutrals); 70% of pesticides and PCB compounds; and 67% of CLP metals. This Region uses GC instrumentation with dual columns, specialized detectors--it has no MS capability.

We envision FASP facilities functioning as more than just a mobile lab, in fact as an overall design composed of base support facilities, support vehicles and instrumentation. The instrumentation can sometimes be moved from the base support unit into a mobile unit, and taken out to the field. When

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the base units and support vehicles were designed, they were intended to be functional as full-fledged labs with interchangeable mobile instruments.

We hope that by this spring, the FASP program will be formed within our Regions with basic facilities, support vehicles and instrumentation which will provide various levels of analytical capability.

To convey some of the cost benefits of using FASP, we compared sample costs in Region X between 1984 and 1988, using capital equipment purchases, facility modifications and upgrades, expendable supplies, and labor costs. The labor costs include documentation, packaging, shipping of samples and QA review. The CLP costs do not include any FASP costs for the analytical system preparation, soil preparation or soil analysis.

In comparing our program with CLP, we do feel that we have a fairly sophisticated level of precision, accuracy, and reproducibility; we feel that some of our savings are real, even though CLP's level of sophistication and documentation are much greater. For our decision making purposes, we always rely on the CLP for a final confirmation. However, there are the real-time and cost savings which are responsible for the considerable support the program receives.

I would like to briefly cite four case studies. The first involved a former electrical transformer salvage yard, for which we had determined that we required about 236 soil samples, (surface and subsurface) to screen for PCBs. The data was to be used to guide subsequent sampling allocation placements and to determine the extent of contamination within the boundaries of this site.

The sample data turnaround ranged from less than one hour to about one day, and the cost for FASP on this particular site inspection was $16,538. This included sample documentation, materials, and labor. Five percent of the samples were sent to the CLP for confirmation. The cost was about $2,100. The FASP cost for work on this site is the equivalent of 53 CLP samples, although the determination had been made that 236 were needed. It is thus evident that our approach reduced the demand on the CLP laboratories.

The second case involved a road oiling facility. One hundred twenty soil gravel samples were needed for PCB analyses. These samples were shipped from Alaska to our facility in Region X. Daily telephone reports provided the on-site officer with daily information for his work. Sample turnaround was a day or less, and the cost from the FASP was $8,409. The cost of the CLP's 10% confirmation (which is typical for our program) was $3,300.

The FASP cost equalled about 26 CLP samples, and we had determined a need for 120 samples. Again, our reliance and demand on the CLP were reduced to about one-quarter of the normal analytical operation cost envisioned for that particular site.

The third case study involved a former creosote facility. The Region determined a need for 500 soil samples, screening them for pentachlorophenol and polycyclic aromatic hydrocarbons.

The sample turnaround time for all of these analyses was three days or less. The cost to our contract through FASP was $91,000, and the CLP cost was about $16,000 or approximately 10%. Yet again, the FASP cost equalled 189 CLP samples, whereas 500 had been projected. Had we used the CLP exclusively, (and received their level of data quality), expenditures would have exceeded the above amount by over $100,000.

Case study number four was a removal site. The FASP benefited by supporting their need for real-time data. In this case, we were required to take 350 multimatrix samples, as well as screening for PCBs, aromatic and chlorinated volatile organic compounds. The FASP data were used to guide removal activities and to verify clean-up action.

Sample turnaround time was 24 hours or less. The cost to FASP was about $79,000, and these FASP costs are equivalent to 138 samples, versus the 350 that we actually took.

There were additional savings at this site which are difficult to quantify. The agency spent approximately $1.3 million over two months at this site, which is about $22,000 per day. By using the FASP program, we were able to complete our work at the site three weeks earlier than we would have without the program's support. This yielded a substantial savings, considering the $22,000 per day cost.

In summary, the key factor in using the FASP program is to use it appropriately.

SCREENING ENVIRONMENTAL POLLUTANTS AND BIOMARKERS: THE ANALYTICAL CHALLENGE

Tuan Vo-Dinh
Advanced Monitoring Development Group
Health and Safety Research Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6101
U.S.A.

ABSTRACT

Detailed characterization of all chemical pollutants in environmental samples from industrial and waste sites is possible using analytical techniques such as liquid or gas chromatography and mass spectroscopy. But for many environmental monitoring programs and assessment applications, these analytical procedures would be needlessly time-consuming and expensive. It is often desirable to have a screening procedure to prioritize environmental samples before detailed analyses are conducted on a subset of samples to reduce the total cost of monitoring programs and environmental studies. This presentation describes the various screening techniques such as synchronous fluorescence (SF), and room temperature phosphorescence (RTP) and provides an overview of advanced analytical techniques and instrumentation such as surface-enhanced Raman scattering (SERS) and antibody-based fiberoptics sensors for use to detect trace levels of chemical pollutants and related biomarkers in complex environmental samples.

INTRODUCTION

The potential toxicity of many chemicals at hazardous waste sites has created an area of great concern. Analysis of complex environmental samples is generally conducted using techniques such as high-performance liquid chromatography (HPLC) or gas chromatography/mass spectroscopy (GC/MS). These analytical techniques, however, are not employed on a routine and systematic basis to study all samples because of the high cost involved. To reduce the total cost of process monitoring or environmental assessment studies, it is desirable to use a screening procedure to rank samples so that a more detailed characterization can be conducted on a select subset of the samples.

This presentation provides an overview of various spectroscopic techniques and state-of-the-art instrumentation for screening environmental pollutants. An important challenge in chemical analysis is the characterization of complex mixtures. Whereas the identification and quantification of a specific compound at trace levels remain important goals, the ability to screen complex mixtures has become a major focus of current research efforts. The importance of complex mixtures has arisen from the need to identify, monitor and understand synergistic and/or antagonistic effects of multi-component systems. Methods such as synchronous luminescence (SL), room temperature phosphorescence (RTP) and surface-enhanced Raman scattering (SERS) are described. The trade-off between selectivity, sensitivity and cost-effectiveness in analysis is presented. Advanced instrumental systems integrating fiberoptics, laser technology and immunochemical methods for potential applications in environmental analysis are discussed. Another area of great importance is the application of analytical techniques to monitoring environmental biomarkers. This is a challenging area for research and development, and advances in analytical methodology and instrumentation are critically needed to analyze complex biochemical systems in the attempt not only to monitor the presence of chemicals in the environment but also to assess the ultimate effects of these chemicals on global ecosystems and on human health. Examples of analysis of chemical and related biomarkers are given to illustrate the usefulness and cost-effectiveness of screening techniques for the analysis of complex environmental systems and for the assessment of human exposure to toxic chemicals.

LUMINESCENCE SCREENING TECHNIQUES

Fluorescence spectroscopy is one of the most sensitive techniques for detecting polynuclear aromatic (PNA) compounds, which are of particular interest in environmental screening programs. These pollutants, many of which are suspected to be carcinogens (1,2), are produced during incomplete combustion of organic materials and are found in many industries, incinerators and waste dump sites.

Because of its higher sensitivity, fluorescence analysis requires less raw material and shorter sampling times than chromatography. This is advantageous for environmental assessment since only small quantities of PNA compounds are obtained by standard extraction methods.

Despite the apparent advantages, fluorescence spectroscopy has been limited in analyzing complex mixtures because the emissions of the various species tend to overlap, yielding spectra with poorly resolved structures. This constraint can be overcome using synchronous luminescence (SL) techniques to improve spectral resolution (3-6).

In conventional luminescence spectroscopy, either the excitation or emission wavelength is varied. In SL, the luminescence signal is recorded while the excitation and emission wavelengths are scanned simultaneously. This improved selectivity by narrowing the targeted spectral bands to reduce emissions from compounds that might otherwise cause interference.

The fixed wavelength interval is ($\Delta\lambda$) is maintained between the excitation and emission wavelengths during the measurement (3,4). In the synchronous fluorescence (SF) approach, the optimum wavelength interval depends on the Stokes shift and is typically 3 nm (4). For synchronous phosphorescence (SP), the optimum interval is determined by the singlet-triplet energy difference and usually ranges from 100 to 300 nm (3). The conventional emission/excitation and the synchronous fluorescence spectra using different $\Delta\lambda$ values are illustrated in Figures 1 and 2 for benzo(a)pyrene.

SL offers instrumentation simplicity. Devices intended for conventional fixed-excitation spectra can often be employed for synchronous measurements with little or no modification. Several spectrometers are available with provision for interlocking the excitation and emission monochromators and the feature can be easily added to many other units. A variety of environmental samples have been analyzed to illustrate the applicability of the SF techniques for screening PNA compounds in waste water (6,7), air samples from industrial (8) and residential environments (9).

Room Temperature Phosphorimetry (RTP):

Conventional phosphorimetry requires the use of low-temperature matrices to reduce the collisional quenching mechanisms and radiationless deactivation processes. Due to the requirement of cryogenic equipment and refrigerant, conventional phosphorimetry has limited usefulness for routine applications in field measurements.

Unlike conventional low temperature phosphorimetry, RTP is based on detecting the phosphorescence emitted from organic compounds adsorbed on solid substrates at ambient temperatures (10). The general approach is to obtain a solution containing the materials to be analyzed using standard extraction procedures. A few microliters of the sample solution are then spotted on a filter paper. The spot is dried for about five minutes with a heating lamp then transferred to the sample compartment of the spectrometer. Measurements can be performed with any commercial spectrofluorimeter equipped with a phosphoroscope (10).

RTP sensitivity and selectivity can be enhanced by mixing the sample of pretreating the filter paper with a heavy-atom salt solution (11). Salts such as thallium acetate, lead acetate, sodium bromide, and cesium iodide are efficient in enhancing

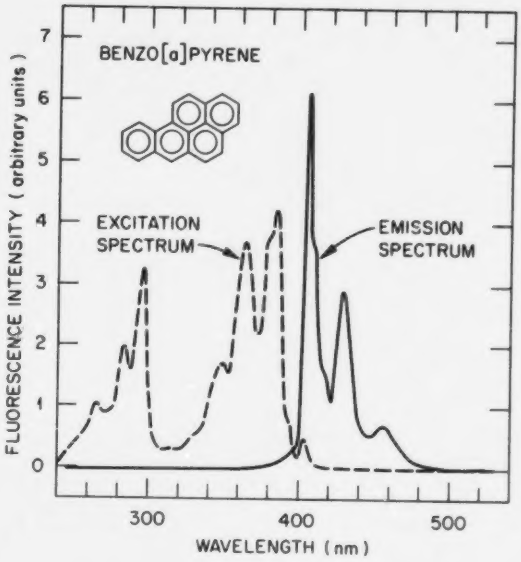

Figure 1. Conventional Fixed-Excitation and Fixed-Emission Fluorescence Spectra of Benzo(a)pyrene.

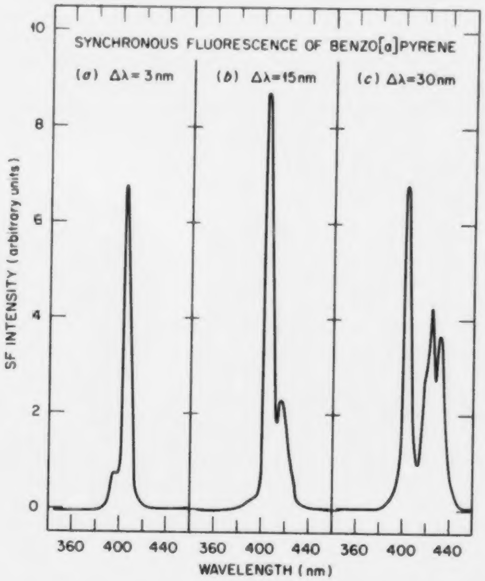

Figure 2. Synchronous Fluorescence Spectra of Benzo(a)pyrene. (The Line-Narrowing Principle is illustrated using various wavelength intervals: $\Delta\lambda$ = 3, 15 and 30 nm).

phosphorescence quantum yields for most PNA compounds.

Figure 3 illustrates the characterization of fluoranthene, a PNA pollutant commonly found in environmental samples, using the RTP techniques. This figure shows the RTP spectra of a coal liquid sample spiked with fluoranthene using thallium acetate as the heavy-atom perturber. The efficacy and cost-effectiveness of the RTP techniques for screening complex environmental samples have been demonstrated in previous studies (9-12).

Although most environmental assessment studies of PNA have dealt with the solid phase, the compounds are also found in the atmosphere as vapors. The vapor phase explains inconsistencies in conventional analysis (13) and creates a need for more direct monitoring methods. The problem is that low concentrations require higher sensitivity than has generally been available.

A simple screening method for PNA vapors involves a passive dosimeter that can measure time-weighted average exposure for periods such as a day. The proposed instrument would be a lightweight finger-size badge, meant to be carried by a worker (14). The sampler might also contain an organic absorbent in a tube. This would set up a vapor concentration gradient down the tube and induce transfer of PNA by diffusion onto the filter paper substrate. The PNA pollutants collected by the filter paper can be detected by RTP.

The PNA dosimeter has been used to monitor individual compounds as well as mixtures under both laboratory and field monitoring situations. Figure 4 illustrates the capability of the dosimeter for detecting quinoline (QUI) and pyrene (PYR) during the field evaluation. The figure shows the RTP response of the dosimeter exposed at different locations a synfuel production plant. The RTP response of a dosimeter placed in a clean room (blank) showed a broad emission.

NEW TECHNIQUES ON THE HORIZONS

Surface-Enhanced Raman Scattering (SERS):

Hazardous pollutants emitted from energy-related technologies, chemical industries, or waste materials are of increasing public concern because of their potential adverse health effects. Many pollutants have chemical groups of toxicological importance that can be characterized and detected by Raman spectroscopy.

Raman spectroscopy, however, has not been widely used in trace organic detection, even though the information contained in a Raman spectrum is most valuable for chemical identification. One limitation of conventional Raman spectroscopy is its low sensitivity that often requires the use of powerful and costly laser sources for excitation. However, a renewed interest has recently developed among Raman spectroscopists as a result of various observations that indicate enhancements in the Raman scattering efficiency by factors up to 10^6 when a compound is adsorbed on or near special

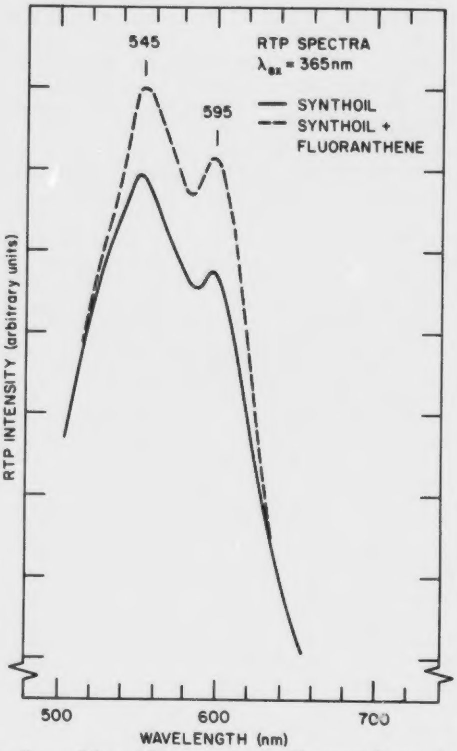

Figure 3. Identification of Fluoranthene in Coal Liquid (Synthoil) Using Room Temperature Phosphorescence Screening Technique.

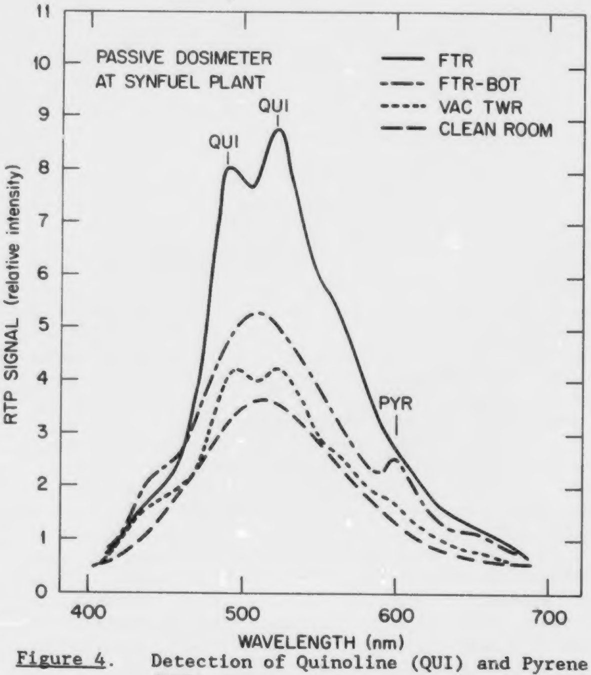

Figure 4. Detection of Quinoline (QUI) and Pyrene (PYR) Vapors Using a Simple Personal Dosimeter at Various Locations in a Synfuel Plant.

metal surfaces. These spectacular enhancement factors of the normally weak Raman scattering process help overcome the normally low sensitivity of Raman spectroscopy. The technique associated with this phenomenon is known as Surface-Enhanced Raman Scattering (SERS) spectroscopy. The Raman enhancement process is believed to result from a combination of several electromagnetic and chemical effects between the molecule and the surface (15).

For the past few years, we have evaluated the SERS technique for environmental applications using practical SERS-active substrate materials based on silver-coated microspheres deposited on glass and filter paper (16-17). A wide variety of organophosphorous chemicals including methyl parathion, fonofoxon, cyanox, diazinon, formothion, and dimethate have been investigated (18). We also report SERS analysis of chlorinated pesticides including carbophenothion, bromophos, idichloran, linuron, chlordan and 1-hydroxychlordene (19). The detection limits for these pesticides were measured at nanogram and subnanogram levels. The results achieved with these chemicals are of great analytical interest since these chemicals are difficult to detect by other techniques such as luminescence spectroscopy due to the weak luminescence quantum yields of these compounds. A mixture of structurally related compounds, and a soil sample contaminated with pesticides were analyzed by SERS to illustrate the selectivity of this new technique as a screening tool for environmental applications (18, 20).

A major advantage of Raman spectroscopy is the spectral selectivity of the technique for the analysis of complex mixtures because of the sharpness of the Raman emission peaks. Figure 5 illustrates this spectral selectivity for the SERS technique for the characterization of a synthetic mixture containing benzo(a)pyrene (BaP), 1-nitropyrene and pyrene (21).

Immunological Techniques and Instruments:

Immunological methods, which offer the capability of excellent selectivity through the process of antibody-antigen recognition, have revolutionized many aspects of chemical and biological sensor technologies. Their high specificity and sensitivity permit the measurement of many important compounds at trace levels in complex biological samples. Radioimmunoassay (RIA) utilizes radio-active labels and has been the most widely used immunoassay method. Immunoassays have been applied to a number of fields including pharmacology, clinical chemistry, forensic science, environmental monitoring, molecular epidemiology and agricultural science (22). The usefulness of RIA, however, is limited by several shortcomings, including the cost of instrumentation, the limited shelf life of radioisotopes, and the potential deleterious biological effects inherent to radioactive materials. For these reasons, there are extensive research efforts aimed to develop simpler, more practical immunochemical techniques and instrumentation which offer comparable sensitivity and selectivity to RIA.

New developments in sensing technology instrumentation, laser miniaturization, biotechnology and fiberoptics research have provided opportunities for novel approaches to the development of sensors for the detection of human exposure to toxic chemicals and biological materials. The development of fiberoptics chemical sensors has been reviewed (23,24, and references therein).

For the last few years we have devoted extensive efforts to integrate immunological methods and fiberoptics technology in order to develop advanced in-situ monitoring instruments for chemical and biological systems. The operating principle of fiberoptics immunofluorescence biosensors has been presented previously (25-27). Examples of measurements will illustrate the application of a laser-based fluoroimmunosensor (FIS) developed for the detection of important biological compounds such as carcinogen metabolites and DNA-adducts of carcinogens. The FIS instrument derives its analytical selectivity through the specificity of antibody-antigen reactions (25,26). Figure 6 shows a schematic diagram of the FIS device (26). Antibodies are contained at the tip of the fiberoptics sensor for use in in-vitro and in vivo fluorescence assays. High sensitivity is provided by laser excitation and fluorimetric detection. An important PNA compound of great interest to toxicologists and cancer researchers is benzo(a)pyrene (BP). Studies have shown that BP is metabolically activated to electrophilic intermediates, which can bind covalently to DNA. A specific diol epoxide derivative of BP, r-7,t-8-dihydroxy-t-9,10-epoxy-7,8,9,10-tetrahydrobenzo(a)pyrene (BPDE) was found as the major carcinogenic metabolite involved in binding to DNA. Metabolized BP is eliminated through the urine and feces. Since the carcinogenic activity of a compound might be associated with the degree to which it binds to DNA, there has been a great deal of interest in analytical techniques that are capable of detecting DNA-carcinogen interactions and thereby leading to a new approach to monitor human exposure to PNA compounds. In this study a new design of the FIS sensor tip was used. The results of investigations employing a fiberoptics FIS designed to measure the BP-DNA adduct product, BP-tetrol (BPT), indicate that the FIS is capable of achieving a 40-attomole (10^{-18} mole) limit of detection for BPT (28).

CONCLUSION

The development of rapid inexpensive screening techniques and instrumentation is critical to decrease the cost of environmental impact studies and human health assessments. Extensive research efforts and resources are required to develop and apply advanced analytical techniques and state-of-the-art instrumentation. However, current efforts are often fragmented and constrained by limited resources. It is our hope that the current awareness for a clean environment will create a strong focus, improved coordination and enhanced collaboration between government institutions (national laboratories, federal agencies), academic

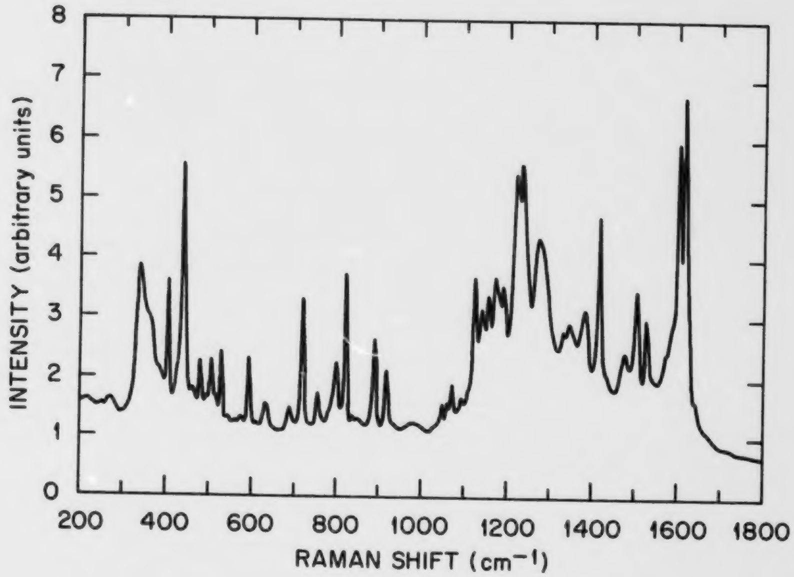

Figure 5. Analysis of a Multicomponent Mixture by Surface-Enhanced Raman Spectroscopy

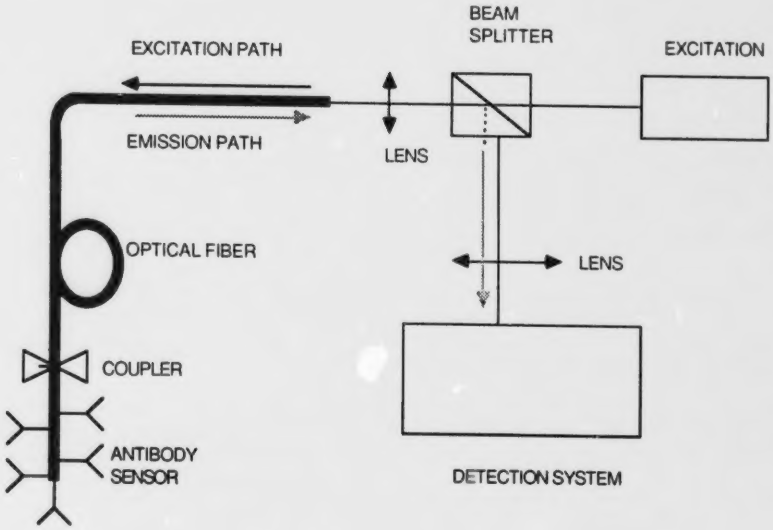
EXCITATION PATH
EMISSION PATH
BEAM SPLITTER
EXCITATION
LENS
OPTICAL FIBER
LENS
COUPLER
ANTIBODY SENSOR
DETECTION SYSTEM

Figure 6. Schematic Diagram of the Antibody-Based Fiberoptics Sensor.

institutions and the private sector in order to achieve the ultimate goal of rapid development and transfer these advanced screening technologies to the user community.

ACKNOWLEDGEMENT

This research is sponsored by the Office of Health and Environmental Research, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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DISCUSSION

ROBERT SNELLING: I have a question, which I believe can be answered by the audience itself. I spoke earlier about wanting to create a partnership between EPA and the private sector, to develop and evaluate technologies which can meet the needs that were discussed this morning. People in the private sector, however, must also consider the economic aspects of the problem. How does it profit the private sector to invest in this program? In order to determine this, they need information similar to that which was presented here. Where can private investors obtain the information they need to decide whether an investment in a given program would be profitable?

SCOTT FREDERICKS: I have an immediate response. My upper management is one hundred percent behind this concept. Our REM and TES contracts all contain options for developing this type of a capability. The FASP is accelerating, and we are going to utilize it within all of our new procurement actions in the future. The private sector also has a strong need to perform a lot of its own sampling and remedial action independently. In that type of arena, the contractors will be relying heavily upon the private sector to provide them with the same cost savings, as it is an important component of their approach to clean-up work.

With these demands on the private sector, the Agency has finally realized the advantages of this sort of approach and is ready to make use of them. I think this symposium is a result of this increased emphasis and acceptance of this approach by all parts of the community, whether academic or governmental. I really believe that there is a viable place in the market for this type of screening. In fact, there is now a small company called Nutriclean, which promotes purity in agricultural products. Apparently this is going to be a trend in the future, among supermarkets, which will attempt to entice customers by claiming that their products – whether fresh or packaged – have been tested for purity. In this way, a lot of in-the-marketplace testing will occur. I think there is a big future in this.

AVRAHAM TEITZ: I wish to know the legal defensibility of the FASP data which was gathered.

SCOTT FREDERICKS: We have been concerned about this issue as well.

We have worked with the contractors who helped us to develop the HRS, because we are concerned about how well it can be used for listing a site, for going forth in the rule-making process. We have also worked with our Waste Programs Enforcement Office to examine whether site data which originate exclusively with FASP can in fact be used in a court of law. In both cases, the answer was yes.

The key is to have a very well-documented approach, using trained personnel who employ certain types of established methods. There must be a standard chain of control or custody. If trained people are employed and standard operating procedures are followed, then nobody will have a problem with the data.

AVRAHAM TEITZ: I also wondered whether quality assurance oversight is in place for the FASP program, similar to that used for the CLP program.

MR. FREDERICKS: Quality assurance is an integral part of FASP, as well. In fact, one of our biggest problems in obtaining support for the FASP process, is obtaining sample standards for field approaches. They are either not readily available, or simply nonexistent, and in some cases, we have had to attempt to produce standards for our own samples that can be used for the instruments which we employ.

By and large we recognize that quality assurance is an important part of this process. If you want more information on the technical approach, the last paper presented in this symposium on Thursday is by Hunt Chapman, who is going to describe the use of the FASP program on several sites, and to discuss this point in detail. Also, Andy Hafferty from Region X in Seattle, who was one of the chemists who helped pioneer this in our Regional office, can provide additional information.

ALISSA HUDSON: Do you consider legal defensibility a mandatory criterion for the use of a field screening method, or do you feel that there are other applications where the method may be helpful, and therefore used, even though the information may not be used in a legally defensible way?

SCOTT FREDERICKS: It is necessary to establish your intended purpose for a given site before you take a sample from it. You may take three or four hundred samples during the course of an overall investigation, half of which may not be of legally defensible quality. However, if you make a final decision to proceed with a listing, or with a negotiation with the PRP, it is essential that you possess data which will support that decision.

RICHARD GAMMAGE: I would like to ask a rhetorical question. I have the impression, which I hope is erroneous, that you have field screening methods completely under control. You have reduced costs, you have an abundance of case histories. What is left for the researcher to do?

ROBERT SNELLING: I think there are a lot of tools available to us, and it has been pointed out that our concern with respect to existing technology is appropriate use of these tools. We seek to develop protocols for their use so that they will be used consistently.

But we are also aware that there are a number of emerging technologies which are not yet commercially available, but offer advancements in our capabilities to do on-site screening. Immunoassay, for example, is a technology emerging from the pharmaceutical industry which offers tremendous potential for on-site analysis. It is difficult to target those assays for the specific analytes in which we are interested. It is a development effort. The technology that you will hear about this afternoon, related to the use of fiber optics, optrodes and laser stimulation, offers a whole range of new tools which could be applied to hazardous waste sites.

Our first task was to identify what is available for immediate use and to evaluate and standardize those methods. The second task is to identify those needs which are not being met and to stimulate evolving technologies that can be applied to the hazardous waste site characterization program.

CARLA DEMPSEY: Managers are often asked at EPA headquarters how good these field screening methods are. These methods are being used to make site decisions, but many users are concerned about their precision, their level of quality assurance. They consider stopping use until these questions are answered completely, which would be a step backwards.

Right now, we are focusing a lot of attention on the users of these methods, to find out what decisions are being made with this data, and to determine the future uses for field screening or analytical methods. We are requesting information about the program's current uses and suggestions for improvements to the program, but we can also develop other applications for these methods from the current information we receive. In gathering this information, we not only define appropriate use for today, and target possible future uses, but attempt to deliver that information back to the private sector and to the researchers who can develop these areas.

MONITORING OF GASOLINE VAPOR AND LIQUID BY FIBER OPTIC CHEMICAL SENSOR (FOCS) TECHNOLOGY

Stanley M. Klainer, Kisholoy Goswami, Don Le Goullon, D. K. Dandge,
Johnny R. Thomas,[a] Stephen J. Simon,[b] and Lawrence Eccles[c]

ST&E, Inc.
1214 Concannon Boulevard
Livermore, CA 94550-6002, USA.

ABSTRACT

Gasoline leakage from underground storage tanks contaminate the drinking water system and poses a severe threat to public health and to the environment. To monitor any intrusions into the ground water and vadose zone, a fiber optic chemical sensor (FOCS) has been developed which measures gasoline as a liquid, a vapor, dissolved in water and as a gasoline-water emulsion. This sensor is based on a special coating which has a high affinity to gasoline. The complete sensor system consists of a portable spectrometer and the gasoline sensor. The components of the spectrometer include a tungsten-halogen lamp as the light source, narrow band filters, a dichroic mirror, a photodiode detector and associated electronics. A fiber optic cable is utilized to direct light into and out of the instrument. The chemical sensing material is incorporated onto the side of a short fiber optic core. One end of this probe is coupled to the long cable and the other end is impregnated with a fluorescent dye. The fluorescence intensity of this dye is modulated by gasoline in the sensing region of the probe. This intensity variation provides quantitative information.

Laboratory results indicate that the gasoline FOCS is specific to gasoline in the presence of such hydrocarbon mixtures as kerosene and jet fuel. Sensitivity covers the range of < 10 μL/L to 100 percent liquid gasoline. Focus has been on the measurement of gasoline vapors as well as the vapors of the individual gasoline constituents. Varying responses are indicated to these components, the substituted aromatic hydrocarbons being more responsive than the aliphatics.

Key Words: Gasoline detection, fiber optic sensor, underground storage tank leak monitor

1.0 INTRODUCTION

There is an existing requirement for a gasoline sensor to monitor: (i) leaking underground storage tanks, (ii) spills, and (iii) between the walls of double liner storage tanks. This capability is urgently needed because the contamination of drinking and ground water by gasoline leaking from underground storage tanks presents a considerable health hazard in the United States. As this directly relates to the availability of potable drinking water, the need to monitor is acute. Early detection of leaking gasoline is imperative as it would not only protect the nation's water supplies, but would prevent costly clean up operations and avoid heavy Government penalties and fines. Under the U. S. Environmental Protection Agency's UST (underground storage tanks) program, monitoring these tanks is mandated [1]. In order for this to be accomplished, the monitor should be able to reversibly detect and quantify gasoline as: (i) a vapor, (ii) a liquid, (iii) dissolved in water and (iv) as a water emulsion. In addition, to be practical the sensor system must be: (i) specific to gasoline and not the individual additives, (ii) sensitive over the range of vapor to 100% liquid, (iii) reliable, (iv) inexpensive and (v) easy to operate. Several attempts have been made to develop a gasoline sensor to meet these minimum requirements [2-6] but none have been successful. A FOCS that appears to meet these criteria is described in this report.

2.0 DESCRIPTION OF THE GASOLINE FOCS

In the design of any FOCS the first criterion is that the device must transmit light. Then it must be able to interact with a target in a known way to give a measurable quantity which can be related to the information desired. For the FOCS, this is governed by the selected chemistry and, therefore, the physical design must support the chosen chemical systems.

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[a] FiberChem, Inc., 3904 Juan Tabo NE, Albuquerque, NM 87111

[b] Lockheed-EMSCO, 1050 E. Flamingo Drive, Las Vegas, NV 89109

[c] Environmental Protection Agency, 944 East Harmon Avenue, Las Vegas, NV 89109

Although, in the final analysis, a FOCS is a rather simple device, its design is complex because it involves many different disciplines such as: (i) chemistry, (ii) fiber optics, (iii) immobilization, (iv) optical spectroscopy and (v) unique instrumentation concepts. Not only are all of those a consideration in the overall development plan, but they must be integrated to make a reliable, rugged, long-lived system which meets the needs for environmental monitoring and, in some instances, diagnostics. The starting point, therefore, is a set of specifications and the end is a field-hardened device.

2.1 REFRACTIVE INDEX FOCS [7,8]

The gasoline FOCS is based on refractive index matching. In these types of sensors the amount of light refracted changes as the analyte interacts with the coated surface. This alteration in light intensity can be directly related to the concentration of gasoline present.

The refractive index sensor consists of a bare fiber optic core with a thin clad of an organic or inorganic compound on its side. In one design the sensor has a fluorescent tip formed with an immobilized dye. An excitation signal is transmitted through the fiber tip and the fluorescence emission is used as a constant intensity light source. This is detected as the return signal. It is also possible to put the excitation source and the detector at the opposite ends of the fiber. A change in refractive index of the medium surrounding the fiber alters the transmission characteristics and results in a variation in the amount of light that reaches the detector. Laboratory test results indicate the ability to quantitate gasoline over a wide dynamic range. The schematic diagram of a gasoline FOCS is shown in Figure 1.

The gasoline sensor consists of a fluorescent dye, such as rhodamine B or fluorescein attached to the tip of the fiber. This is done with the help of a UV curing glue. A 2-cm long coating of a proprietary material, with selective high affinity for gasoline is incorporated on to the side of a fiber core at its distal end. In the absence of gasoline, the returning light has a high intensity because air (or water) has a smaller refractive index than the core, whereas, in the presence of gasoline, the intensity of the return signal becomes reduced because of the higher refractive index of the analyte.

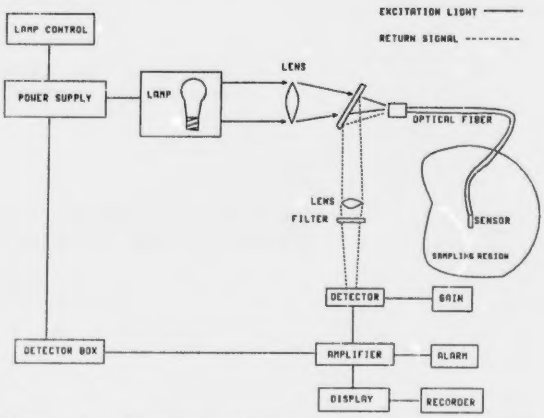

Figure 1: Schematic Diagram of a Gasoline FOCS System

The intensity of the return signal decreases proportionately to the amount of gasoline present, due to the modulation of the fluorescent light. This gasoline FOCS has the following characteristics: (i) it responds to liquids, vapors, dissolved gasoline and gasoline-water emulsions; (ii) it has wide dynamic range, i.e. percents to <10 μL/L; and (iii) it operates in either the alarm or quantitation mode. Furthermore, this technology can be extended to the measurement of other species.

3.0 SUPPORT INSTRUMENTATION [9,10]

The Fiber Optic Chemical Sensors are designed so that specificity to a particular molecule or class of compounds is relegated to the sensor chemistry and, therefore, only the intensity of light coming out of the fiber and its wavelength need to be assessed. Consequently, it is possible to use a very simple device to make these measurements. The complete sensor system consists of: (i) a tungsten-halogen lamp for a light source; (ii) the gasoline FOCS; (iii) a spectral sorter; (iv) a photodiode detector; (v) signal collection, processing and display electronics and (vi) a readout (meter or recorder).

4.0 RESULTS AND DISCUSSION

The gasoline sensor was tested in the laboratory against: (i) liquid gasoline, (ii) gasoline vapor, (iii) gasoline dissolved in water and (iv) some of the individual volatile gasoline components. Figure 2 shows the response of the FOCS to liquid gasoline and vapor. This experiment was performed by using an argon-ion laser as the excitation source (514 nm) and a photomultiplier tube detector in combination with photon counting equipment. It is important to note that the sensor is completely reversible and this indicates that only a physical interaction is taking place between the coating and the gasoline. Further testing shows that this sensor responds preferentially to gasoline and not to kerosene and jet fuel.

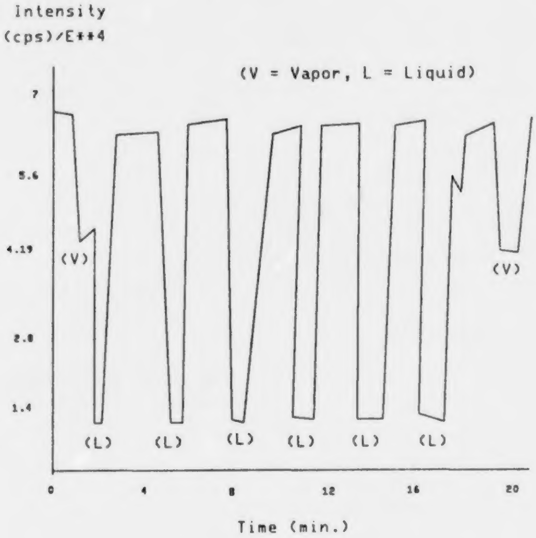

Figure 2: Reversibility of Gasoline FOCS (Computer Trace of Actual Spectrum)

4.1 RESPONSE OF FOCS TO GASOLINE VAPORS

Several brands of unleaded, regular and super unleaded gasoline samples have been measured in the vapor state. Each brand has its characteristic distribution of the components and consequently slopes of the response curves are different. Chevron gasoline, however, has been measured in the most detail. All samples were made up and measured at ambient temperatures. The results obtained for Chevron gasoline concentrations between 1 and 50 μL/L are shown in Figure 3. The term V/V_0 is the normalized response of the gasoline sensor when various concentrations (μL/L) of gasoline are present and V_0 is the voltage reading with no gasoline (7 volts). V is the final voltage reading. Figure 3 shows the response of the FOCS in samples where gasoline was allowed to equilibrate with the air over 24 hours.

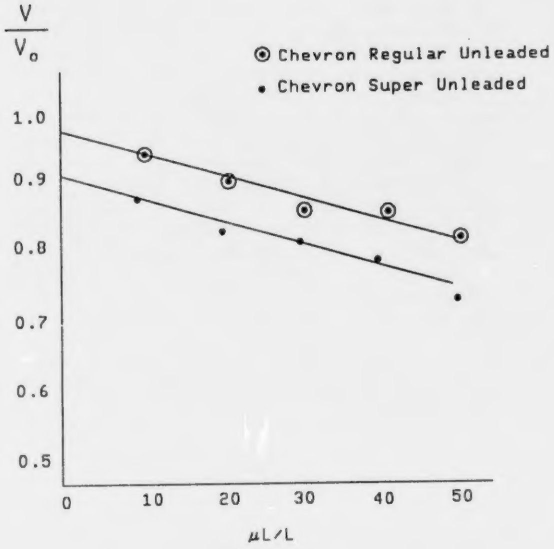

Figure 3: Response of FOCS to Chevron Gasoline Vapors (24-Hour Equilibrium)

4.2 RESPONSE OF FOCS TO GASOLINE DISSOLVED IN WATER

Preliminary experiments were undertaken to determine if the FOCS could see gasoline dissolved in water. This was considered a good test of the sensitivity of the FOCS because the solubility of the key constituents of gasoline is in the low μL/L range. Water and Chevron unleaded regular gasoline mixtures (2:1) were made and then shaken vigorously in a separatory funnel to give a saturated solution. The undissolved gasoline was removed and the water fraction sealed and allowed to stand for twenty four (24) hours. The center portion of the water solution was then analyzed by the FOCS. The results indicated approximately 13 μL/L of gasoline in the water when the response was compared to that of the twenty four (24) vapor phase response. Future testing will include repeating the experiments with the saturated solutions as well as those with less gasoline in them while independently analyzing the individual water-gasoline mixtures with a mass spectrometer.

4.3 RESPONSE OF FOCS TO INDIVIDUAL GASOLINE COMPONENTS

Since gasoline is a mixture of hydrocarbons, it is very important to know if the FOCS is responding preferentially to one or more of the components of gasoline.

To determine this, nine (9) of the key constituents found in all gasolines were measured using a FOCS. Each of the test samples was prepared from compounds purified to spectrographic standards. Forty (40) μL/L vapor samples were made for each species and measured with the sensor after they were allowed to come to equilibrium for three (3) hours. The results are listed in Table 1. The three (3) hour equilibrium response for Chevron gasoline is also shown in Table 1 for reference. Those compounds whose responses were (ΔV) more than gasoline are the ones which respond best to the gasoline FOCS, i.e. the substituted aromatics. Figure 4 shows more detailed data for four of the key aromatic hydrocarbons between 10 and 50 μL/L.

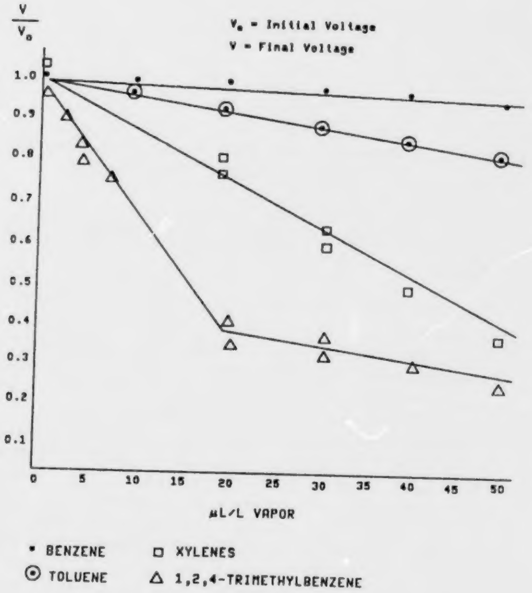

Figure 4: Response of FOCS to 10 to 50 μL/L Vapor of Aromatic Hydrocarbons

TABLE 1

Response of a FOCS to 40 μL/L of Individual Gasoline Constituents

3 hrs.

Gasoline Constituent	V_o-V (V_o = Initial Voltage)	Refractive Index (20°C)	Formula Weight	Boiling Point (°C)
2-Methylbutane	0.133	1.354	72	30
n-Pentane	0.161	1.358	72	35-36
n-Hexane	0.333	1.375	86	68-69
2,2,4-Trimethylpentane	0.462	1.392	114	98-99
n-Octane	1.467	1.398	114	125-127
Cyclohexane	0.396	1.426	84	81
Toluene	1.243	1.496	92	110
Xylene	5.460	1.497	107	137-144
1,2,4-Trimethylbenzene	6.517	1.505	120	168
Gasoline	1.687			

5.0 CONCLUSION

The use of fiber optic sensor for monitoring gasoline has several major advantages over other approaches being used. These are: (i) real time response, (ii) specificity and sensitivity, (iii) remote performance and (iv) portable. Further experiments are being pursued in our laboratory for improving the efficiency of the FOCS system.

6.0 ACKNOWLEDGEMENTS

The authors wish to thank FiberChem, Inc., of Albuquerque, New Mexico 87111 for financial support; Leuren Moret of ST&E, Inc., for preparing the fiber optic chemical sensors (FOCS) and assisting with the laboratory evaluations; and Nelson Herron of Lockheed-EMSCO for collaborative independent testing.

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DISCUSSION

UNIDENTIFIED PARTICIPANT: You wrote you had ice.

STANLEY KLAINER: We can tell the difference between water, ice, and ice crystals, that is, ice at its formation.

UNIDENTIFIED PARTICIPANT: There was really no interference regarding your benzene detector?

STANLEY KLAINER: I can't answer that question completely. I suspect that there is some interference, but we're not sure at this point. We're just beginning. The sensitivity is where we want it, and now we'll start worrying about interferences.

And of course, if the interferences are such that because of the specificity to the benzene – the ability to absorb the benzene and not absorb other things as well – we may overcome the interferences in that manner. That's one of the tricks of picking the right coating.

UNIDENTIFIED PARTICIPANT: So we have two selective processes?

STANLEY KLAINER: Yes. The refractive index only detects the light leak. A mechanical absorption technique is necessary to obtain specificity and sensitivity.

JOHN SCALERA: I have two questions about this. First, what about the stability of the instrument out in the field, since it is dependent upon an optic system?

Second, do you use monochromatic radiation in a fiber optic system to be species specific? I know you identify species on the outer coating on a fiber optic. Do you also use monochromatic radiation to enhance that?

STANLEY KLAINER: First, about the stability of the optics. Obviously, if there are wide temperature swings there are shifts, and you accommodate them by using things such as feedback loops, which monitor the amount of light going into the fiber all the time. That is where the problem is – at the light transmission.

Regarding the question about the species specificity, you could use monochromatic light if you wanted to do some additional spectroscopy. We are not doing it at the present time. We have been able to find sensing materials which seem to be sufficiently specific.

The light is monochromatic, but it's chosen more for where it excites the sample, or where we can detect it best, rather than for its spectroscopic information content at this point.

JOHN SCALERA: Is there any problem with the focusing system on a box system out in the field going out of alignment, or do you have solid state technology?

STANLEY KLAINER: There is always the possibility over large temperature swings of optics going out of line.

If you sample the signal in the right places, and compare them (essentially use a double beaming system) you correct for it internally. You can then do some tricks like chopping it. Or for instance, if you were going to run a system that you knew was always going to be out in the desert, you might seriously consider keeping the box at one hundred degrees the whole time, eliminating the temperature swing.

You have options you can play with, you have to face the questions about what the temperature does to the fiber optic, too. After all, some of the physical sensors are based upon light transmission, which are what temperature sensors are made of. You need to correct for the temperature effects in the fiber optic, as well for the temperature effect in the instrument.

UNIDENTIFIED PARTICIPANT: We used a bulk optics device last year in about one hundred and twenty degrees, and we saw no differentiation of signals between the lab and the field. Properly designed bulk optics seem to work fine.

JOHN EVANS: I'm intrigued by that cyanide sensor. Have you determined whether it is responsive to complex forms of cyanide, or simply free cyanide?

STANLEY KLAINER: I'm going to let Dr. Goswami, who made that sensor, answer the question.

KISHOLOY GOSWAMI: Right now, these sensors are the irreversible, integrating type.

MAHMOUD SHAHRIARI: Regarding the aromatic hydrocarbons sensors you have made, I got the impression that the coatings you are using are actually acting as chemical indicators?

STANLEY KLAINER: No, the coatings do two things. They have preferential mechanical sensitivity to the compounds we're looking at, so that makes them reversible. They are also index matched, so that as the refractive index of this aromatic mixture coating changes, more or less light leaks out of the side of the fiber, and you get a change in signal.

MAHMOUD SHAHRIARI: So it is correct to say you are not using any chemical indicators?

STANLEY KLAINER: No chemical indicators. One of the reasons that we're not using chemical indicators is because we're really worried about bleaching of fluorescent compounds.

There is a dye on there, but it is on the tip, and its only function is as a light source. The tip of the fiber has a fluorofluor on it, in very large amounts that will never bleach, whose purpose is to give us one color light in and one color light out, so we can distinguish between the light color in and the light color out.

THE SUITABILITY OF SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS) TO FIBER OPTIC CHEMICAL SENSING OF AROMATIC HYDROCARBON CONTAMINATION IN GROUNDWATER

Michael M. Carrabba, Robert B. Edmonds, Peter J. Marren and R. David Rauh
EIC Laboratories, Inc., 111 Downey Street
Norwood, Massachusetts 02062

ABSTRACT

A general need exists for chemical sensors to monitor the presence, evolution and hydrological transport of aromatic hydrocarbon contamination in oceans, surface and ground waters. In the most favorable configuration, a chemical sensor should operate in situ and produce quantitative information in real time with a high level of sensitivity. We are investigating the development of a prototype fiber optic chemical sensing probe based on Surface Enhanced Raman Spectroscopy (SERS) on electrodes. The SERS signal is obtained from the Raman scattering of a molecule absorbed onto a roughened metal substrate. The metal substrates that we have investigated with the fiber optic SERS probe (FOSP) are electrodes made of Ag. With this technique, the SERS-related phenomena that are chemically specific, such as the adsorption of organic molecules on metal substrates and the potential dependence of electrosorption, have increased the selectivity. Our results indicate that the FOSP has the capability of providing information about in situ organic contamination that is both sensitive and selective.

INTRODUCTION

"Universal" chemical sensors are needed for the detection and monitoring of toxic substances in the environment. Ideally, such a sensor would produce information in real time about their presence in low levels and their chemical structures. In situ techniques for chemical analysis of aromatic hydrocarbon impurities in water are limited. Specific conductance measurement made in situ are useful in detecting general levels of ionic contamination, but are not species specific. Recent advances in the area of chemically selective fiber-optic sensors or optrodes have shown the usefulness of fiber optic spectroscopic probes for the detection of groundwater contaminations (1,2). But, optrodes are usually specific for a particular compound. Fiber optic probes have been suggested for laser-induced fluorescence monitoring of some organics (e.g., benzenoid hydrocarbons, fluorescent dye "tracers") (2,3). This technique, along with remote fiber optic UV-visible absorption spectroscopy (4), is useful in determining the presence or absence of general classes of pollutants, but yield little direct structural information. Thus, these spectroscopic methods are therefore most useful when a known species or class is being sought which has appropriate absorption or luminescence properties.

Our approach to this problem has been to sample dilute chemical species by adsorption onto surfaces and then to identify the adsorbates by Surface Enhanced Raman Spectroscopy (SERS)(5). The combination of pre-concentration of dilute species due to specific adsorption, and up to 10^6 signal enhancement of SERS over normal Raman spectroscopy, should enable detection well below the parts per billion level. Raman techniques utilize visible light to obtain structurally unique vibrational spectra. Thus, measurements can be made in media such as water with high infrared absorption. In principle, laser Raman excitation and scattering signals can be transported through optical fibers for sampling remote or hazardous environments.

We have previously reported the feasibility of using the SERS technique for the detection of organic water contaminations (5), but the adapting of optical fibers to a truly remote fiber optic SERS probe (FOSP) has not been reported. However, there have been numerous reports of fiber optic probes for normal Raman sampling (6-14). In this paper, we present results on configuring an optical fiber delivery/collection system for conducting remote SERS on electrode surfaces and the development of remote FOSP.

EXPERIMENTAL

All results were obtained using a Raman instrument incorporating a Spex Industries Triplemate spectrograph and an EG&G Optical Multichannel Analyzer for detection. The excitation source was a Coherent Model 70-4 argon ion laser which also was used to pump a Coherent 599-01 dye laser. Unless otherwise indicated, an excitation wavelength of 575 nm was selected using the dye laser, and the intensity leaving the exciting fiber was 100 mW. Electrochemical instrumentation and roughening of Ag electrodes for SERS has been described elsewhere (5). All spectra are shown at an electrode potential of 0.6V vs. a SCE.

The fiber optic probes were constructed with all-silica optical fibers (NA = 0.22) and microbore polyimide tubing from Polymicro Technologies.

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Fiber Optic Probe Design

The design of the fiber optic probe incorporated a small excitation fiber and four large collection fibers. A theoretical calculation of Plaza et al. (6) has indicated that a system would have a higher collection efficiency if the excitation fiber was small and the collection fiber was large. For example, the efficiency of collection in water for a 600 μm diameter fiber goes from 0.065 sr with a 600 μm excitation fiber to 0.132 for a 100 μm diameter excitation fiber. They calculated an optimal efficiency of 0.44 sr for a small excitation/large collection (SELC) system that incorporated a 100 μm excitation fiber with four 600 μm collection fibers. They have also indicated that the efficiency could be increased to 0.7 sr if the collection fibers were placed at an angle of 11 degrees.

The SELC designs are dependent on the overlap of the cones of acceptance of the collection fibers. Figure 1 shows the overlap of the acceptance cone of the collection fibers with the cone of transmission of the excitation fiber for the SELC design of Plaza et al. using angled and non-angled collection fibers. The overlap begins at a distance of 750 μm from the collection fiber surface for the non-angled design and at 380 μm for the angled design. For efficient fiber optic SERS, the substrate should be placed in the overlap region of the collection fibers. The size of the illumination pattern (i.e., spot size) increases as the distance from excitation fiber to substrate increases, thus the spot size would be greatly increased over a normal Raman excitation system (spot size approximately 30 μ). For the non-angled system, the minimum spot size (i.e., the point where the acceptance cones of the collection fibers overlap) would be ∿500 μm while the angled system would have a minimum spot size of ∿300 μm with an unterminated excitation fiber. In order not to waste the excitation light, the area of the substrate should be greater than or equal to the area of illumination.

Experiments have indicated that SERS from a small area (30 μm spot) of a surface is more than adequate for sensor applications (5). A small surface area in our probe should provide an increase in collection efficiency, and it would also add to the compactness of the probe. We attempted to reduce the size of the illumination spot by placing a lens at the end of the excitation fiber. One common method is to mount a microsapphire ball at the end of the fiber (1). This method would not be applicable to our probe, since the mounting mechanism would interfere with our collection fibers. Instead, we employed a more practical way of lensing the end of the excitation fiber, the laser microfurnace technique of Russo and co-workers (15). With this technique, laser light is passed through the fiber to a target material which absorbs the light. The light is then readmitted as infrared light which is capable of melting the tip of the silica optical fiber into a lens. These types of lenses are capable of producing spot sizes of approximately half the fiber diameter. In our optimization experiments, we evaluated the collection efficiency of the assembly illustrated in Figure 1 using such lens-ended excitation fibers.

SELC Probe Fabrication Details

In order to construct an optimum SELC probe for SERS, several factors which complicate the measurement of SERS using optical fibers were addressed. First is the background fluorescence obtained from polymeric fiber claddings. Second is an intrinsic Raman scattering of silica arising from the exciting fiber which is reflected back into the collection fibers from the SERS substrate. In addition, an unstructured background signal is always present in SERS.

The background fluorescence was easily solved by switching to silica cladding. Plastic clad silica fibers were not used due to a broad fluorescence signal that appeared with laser wavelengths greater than 575 nm. The other complications have been addressed by investigating the effect of distance of the collection optics to the SERS surface, the positioning of the excitation fiber as well as the effect of lens-ending the fiber. The placement of the exciting and collection fibers can alter the magnitude of the background signal, since it relates to the intensity of the exciting source (both Rayleigh and silica Raman scattering) reflected back into the collection optics.

The use of lens ended excitation fibers and angled and non-angled collection fibers were studied for the fiber optic excitation/delivery system. All of the SELC probes reported in this investigation have been silica clad. The SELC probes were constructed with a central 100 μm excitation fiber (both lens and non-lens ended) surrounded by four 600 μm collection fibers. The four outer fibers were sealed in opaque epoxy around a microbore polyimide capillary tube large enough to accept the exciting fiber. The array of collection fibers were constructed in configurations parallel to the central fiber and at an angle of 11°. The probes have been embodied into bundles that allow easy coupling of our SERS probe to the spectrograph and to the laser.

Optimization was carried out for a known SERS system of an Ag electrode and 0.05M and 0.02M pyridine at an excitation wavelength of 575 nm. A micrometer was used to adjust the distance between the fiber bundle array and the substrate. In addition, the distance between the central fiber and the substrate was also adjusted.

SELC Experimental Results

Figure 2 is the SERS spectra of pyridine as a function of the distance of the collection optics to the SERS electrode surface for an angle type SELC fiber probe. The results indicate that the optimum position of the collection optic for the angle SELC probe is 2.5 mm. The results for the non-angled SELC probes indicate an optimum distance of 1.9 mm. In comparing the angled and non-angled SELC (Figure 3), a significant increase in the SERS signal intensity was realized by adjusting the collection fiber acceptance angle. Depending on the other variables, this gives up to a 15-fold increase in the SERS signal level compared to a non-angled orientation of delivery and collection fibers. At the same time, enhancing the collection in this way increased the overall background level by a factor of 3 and the silica Raman scattering level by a factor of 7.

Enhancement of the overall resolution (ratio of SERS signal to the silica background) in some cases was accomplished by placing the excitation fiber close to the SERS substrate. The levels of background scattering and silica Raman peaks were evaluated with the excitation fiber position approximately 0.1 mm above electrochemically roughened SERS-active substrates. The results indicate that the background Raman signal from the silica fibers was reduced if the excitation fiber was placed nearly touching the SERS surface, while the SERS signal was relatively unchanged. The effect was observed regardless if there was a lens on the end of the excitation fiber. The reduction in the background silica signal was observed for all the SELC probe configurations. Figure 3 compares the results of the excitation fiber positioning for the SELC probes.

The reduction in background Raman signal is probably due to the way the light exiting the fiber is directed off the SERS surface. When the fiber is close to the surface, the directional light (both silica Raman and Rayleigh) can be reflected back up the excitation fiber, while the SERS signal is isotropic and is thus only affected by the position of the collection fibers.

Our results indicated that the 11 degree angle SELC bundle placed 2.5 mm above the surface with or without a lens ended excitation fiber nearly touching the surface is favored over the other type of probes. One problem with this design is the fabrication of the probe. The assembly of the probe requires bare (no jackets or mounts) fibers. In order to have a good collection surface, the fiber should be polished. But the polishing of bare fibers is not easily accomplished and thus cleaved fiber ends must be used. In addition, extreme care must be taken during the assembly of the probe so the cleaved surface will not be damaged by epoxy or breakage. To reduce the assembly complication, a fiber probe was constructed that had the collection fibers at an 11 degree angle and the end completely encased in epoxy. The end was then polished so that the face of the bundle was flat. Figure 4 shows the comparison of the 11 degree probe with and without the end polished flat. This result indicates that there is an insignificant reduction in collection efficiency when the end of the angle probe is polished flat. Thus, the 11 degree angle SELC can be assembled in both a timely and simple fashion.

Experiments were conducted to determine problems that might arise due to the length and type of optical fiber. Two types (low OH and high OH) of silica/silica clad fibers (Polymicro Corp.) were investigated. Experiments using the Raman spectroscopy of a neat crystalline naphthalene sample at 625 nm and 46 meters of the low OH excitation fiber indicated an extremely high background (Figure 5a). The background from this fiber was so intense that it obliterated the Raman spectrum of the naphthalene. The high OH fiber, on the other hand, produced a good spectrum (Figure 5), but large silica bands were still present at this length.

The large silica background may be due to the silica Raman bands which are travelling as cladding modes in the optical fiber. The signal travelling in the cladding can be easily removed by coiling the excitation fiber around a circular rod. We determined that coiling the excitation fiber around a 1/2" diameter rod was sufficient to remove the cladding modes while not dramatically reducing the total power transmitted by the fiber. Figure 6 shows that a few coils of this excitation fiber greatly reduced the silica noise bands by 46% while reducing the incident laser power and signal strength of the naphthalene Raman bands by only 5%.

Fiber Optic SERS Probe (FOSP)

Two types of fiber optic SERS probes (FOSP) were constructed with the housing material of 3/4" black delrin rod. In the first design, the top half contains the fiber bundle and a Pt counter electrode, while the bottom half contains a Ag electrode substrate and a reference electrode. The latter are connected electrically to the top half by external wires. The bottom half also contains a reservoir for electrolyte which communicates with the outside by a sieve-like array of holes. The electrochemical control of the substrate enables repeated renewal of the substrate surface, and also for control of the adsorbate species, coverage and molecular orientation by electrode potential. This design was suitable for laboratory use, but it does not allow for the easy interchangeability of the SERS electrode. The second type of probe design which used pin connectors to electrically connect the electrode segment of the probe to the fiber section was also investigated. Pin connectors were attached to the working and reference electrode leads in such a way that they can be separated and connected again while remaining insulated from solution. The pin connector design is preferable because the working and reference electrodes are more easily changed. To maintain proper cycling conditions, the fixed pin connectors must be isolated from the solutions.

FOSP Experimental Results

Our experimental results on our FOSP are very encouraging. Figure 7 shows the SERS spectra of pyridine as a function of electrode potential. The electrode was cycled five times between the usual oxidation/reduction cycling (ORC) limits of -0.6 to +0.2V vs. SCE. We tested the renewability of the SERS probe by monitoring the SERS signal from several of the peaks, a function of repeated ORC cycling. Figure 8 shows the signal intensity of the 1006 cm^{-1} as a function of 62 ORCs. The cycling does not significantly affect the ability to observe the SERS spectrum. In fact, we placed over 200 cycles on this SERS electrode with no significant loss of signal. This result indicates the long-term stability of our SERS probe is probably very good.

A contamination problem with our FOSP intermittently appeared at potentials of about -0.2V or higher when cycling in certain solutions. This peak normally disappared at lower potentials (about -0.6 to -0.7V). The contamination is probably from the black delrin plastic used to make the probe. The peak does not appear when other materials are used. Current probe designs are incorporating Teflon.

The effect of changing the cycling conditions of an Ag electrode was examined with the FOSP. The cycling conditions are important especially in the case of in situ renewability and durability of the electrode surface. Electrodes were cycled in pyridine solutions which contained either 0.1M KCl or tap water. The effect of preroughening (i.e., precycling) the electrodes in 0.1M KCl before placing it in the solution of interest was also examined.

A freshly polished 1 mm diameter Ag electrode was preroughened by precycling 3 times in 0.1M KCl with an oxidation/reduction cycle (ORC) of -0.7 to 0.2 volts vs. a silver/silver chloride reference electrode. After cycling, the solution was removed and replaced with 0.02M pyridine in 0.1M KCl. Initially, a weak SERS signal from pyridine appeared (Figure 9a) with the electrode at open circuit. When a potential of -0.7V was applied, the signal improved (Figure 9b). The FOSP was cycled again with the same limits as the precycling and the SERS signal dramatically improved (Figure 9c). This same electrode was removed from solution and washed with methanol and water. The Ag electrode was then placed in a solution of 0.02M pyridine in 0.1M KCl. The SERS signal appeared without recycling the electrode (Figure 9d). After cycling with the previous limits, the signal increased (Figure 9e) but was slightly less than in Figure 9c.

It was determined that in the case of low ionic strength solutions, stopping the cycle at 0.2V for various times before cycling back down to -0.7V improved the signal. The signal improved as the time held at the upper potential increased (Figure 10). Times longer than 20 minutes were not investigated. The most practical time seems to be about 10 min.

A preroughened Ag electrode in a solution of 0.02M pyridine in tap water was also examined. Tap water was used to approximate a low ionic strength condition. The best signal was obtained after cycling and holding at 0.2V for 10 min. An experiment to determine if freshly polished electrodes could be cycled (i.e., roughened) in the tap water solutions of pyridine was also conducted. The SERS signals obtained by cycling only in 0.02M pyridine in tap water were compared with those obtained from a different freshly polished electrode which was preroughened in 0.1M KCl. The results (Figure 11) indicated that the non-preroughened electrodes gave a signal which was half of the preroughened. Even though the signal was half than that observed with the preroughened electrode, the signal level was still very useful.

The results of the cycling experiments indicate that Ag electrodes can be very durable and sustain repeated ORC. The results also indicate that preroughened electrodes would be an advantage in an in situ application (low conductance).

CONCLUSION

Presently, no remote fiber optic chemical sensor exists for the analysis of organic compounds in environments which has both the sensitivity and universal selectivity of the SERS technique. A major limitation to the effective application of SERS or any other Raman based technique is the present stage of development of Raman based instrumentation. In order to apply the SERS technique to a fieldable chemical sensing instrument, future research should be directed at the development of a small and low power consuming system that could operate in a field or laboratory site.

ACKNOWLEDGMENT

This work was supported by the Office of Health and Environmental Research and Ecological Research Division of the U.S. Department of Energy under SBIR Contract No. DE-AC01-86ER80333.

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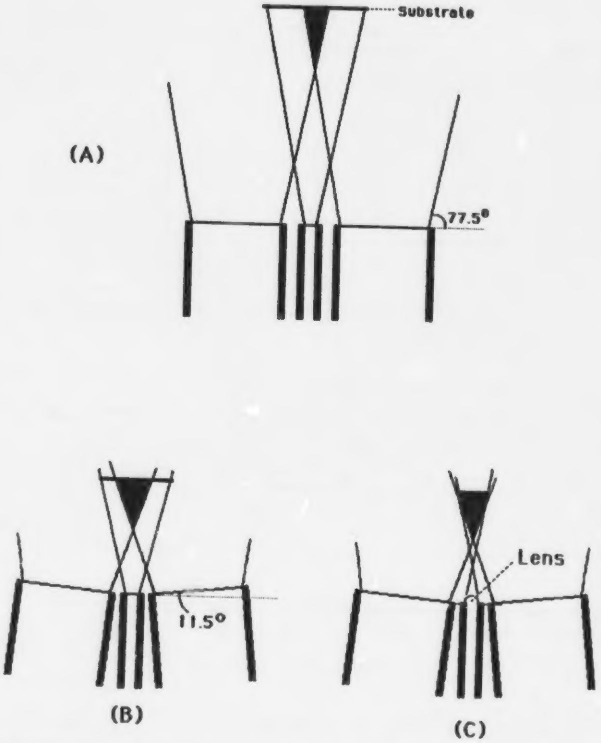


FIGURE 1. RELATIONSHIP BETWEEN FIBER ORIENTATION AND MINIMUM SUBSTRATE SIZE FOR 100 μm EXCITATION AND 600 μm COLLECTION FIBERS: (A) NON-ANGLED; (B) ANGLED AT 11.5°; (C) ANGLED WITH A LENS ENDED EXCITATION FIBER.

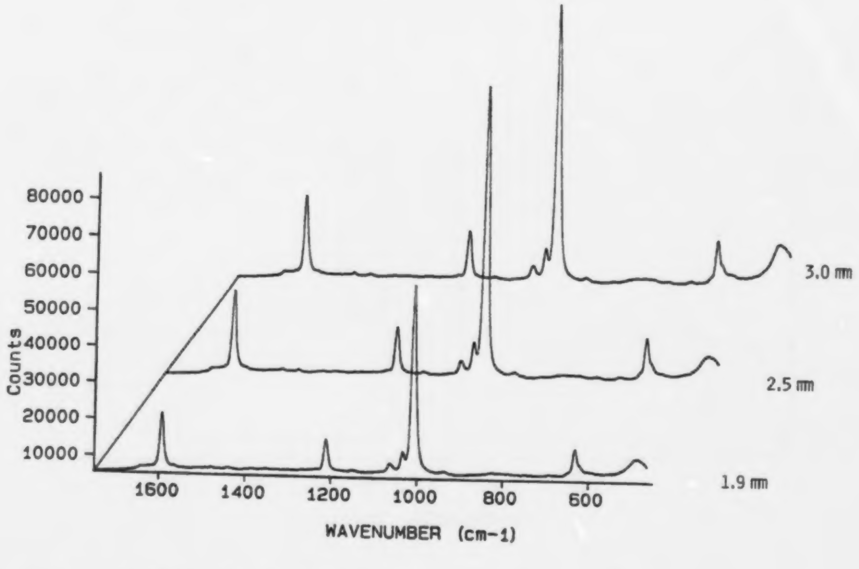
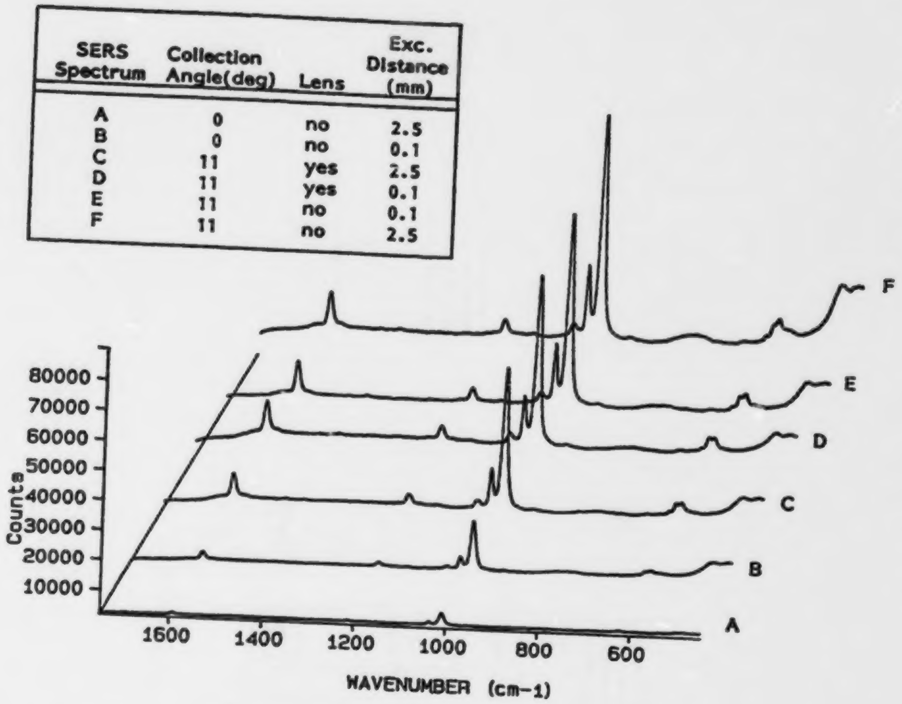


FIGURE 2. THE SERS SPECTRA OF PYRIDINE (0.05M) AS A FUNCTION OF THE DISTANCE TO THE SERS SURFACE FOR AN ANGLED SELC.



SERS Spectrum	Collection Angle(deg)	Lens	Exc. Distance (mm)
A	0	no	2.5
B	0	no	0.1
C	11	yes	2.5
D	11	yes	0.1
E	11	no	0.1
F	11	no	2.5

FIGURE 3. SERS SPECTRA OF 0.025M PYRIDINE ON Ag ELECTRODE.

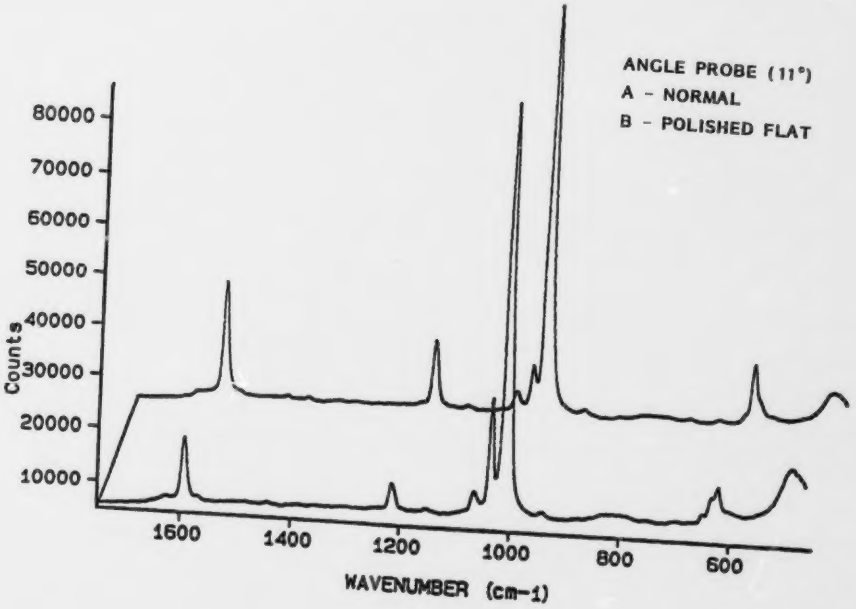


FIGURE 4. THE SERS SPECTRA OF PYRIDINE AS A FUNCTION OF THE END FINISHING OF THE 11 DEGREE ANGLE WITH (B) AND WITHOUT (A) A POLISHED FLAT FACE.

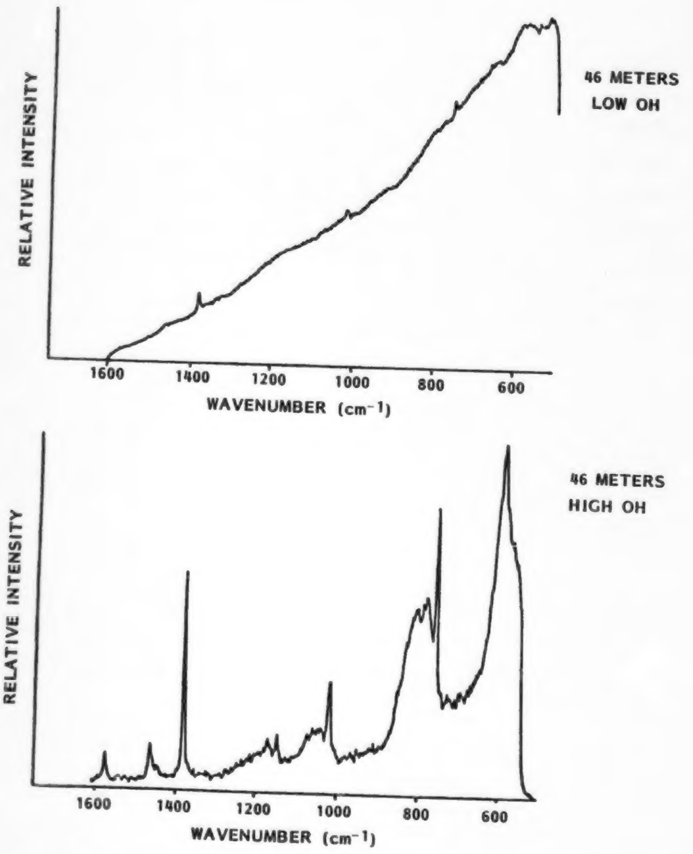


FIGURE 5. THE RAMAN SPECTRA OF CRYSTALLINE NAPHTHALENE USING 46 METERS OF HIGH AND LOW OH CONTENT EXCITATION FIBER AT 625 nm.

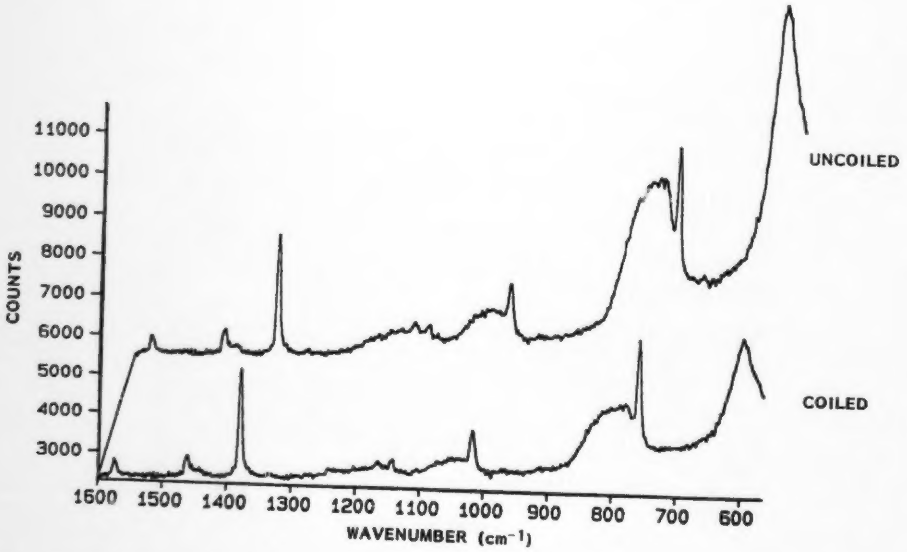


FIGURE 6. THE EFFECTS OF COILING THE EXCITATION FIBER ON THE RAMAN SPECTRA OF CRYSTALLINE NAPHTHALENE USING 46 METERS OF HIGH OH FIBER.

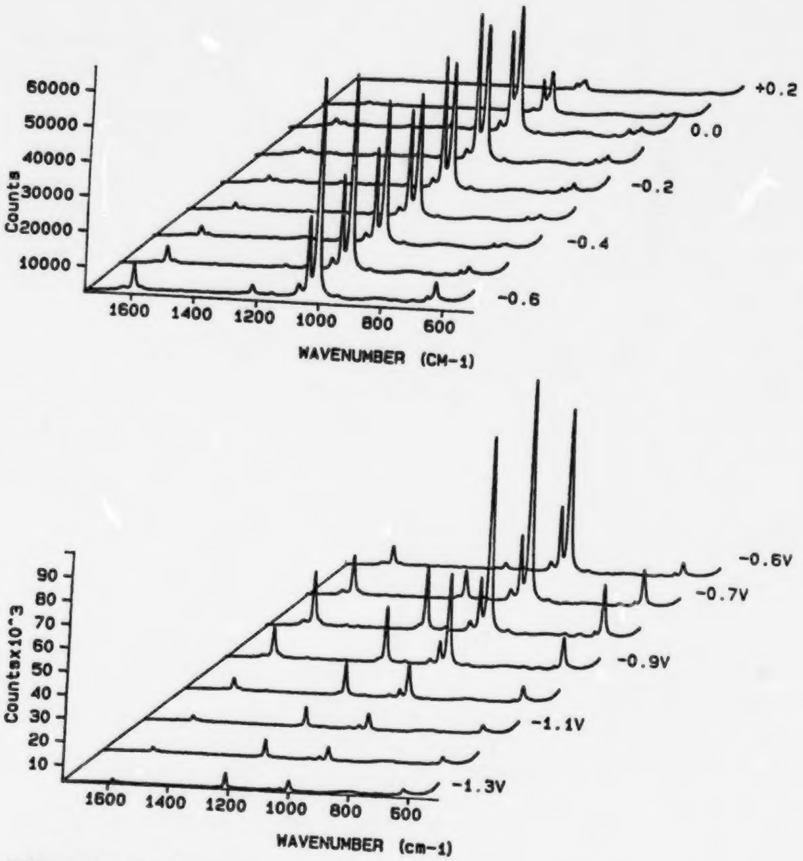


FIGURE 7. THE SERS SPECTRA OF PYRIDINE (0.05M) FROM THE FIBER OPTIC SERS PROBE (FOSP) AS A FUNCTION OF ELECTRODE POTENTIAL.

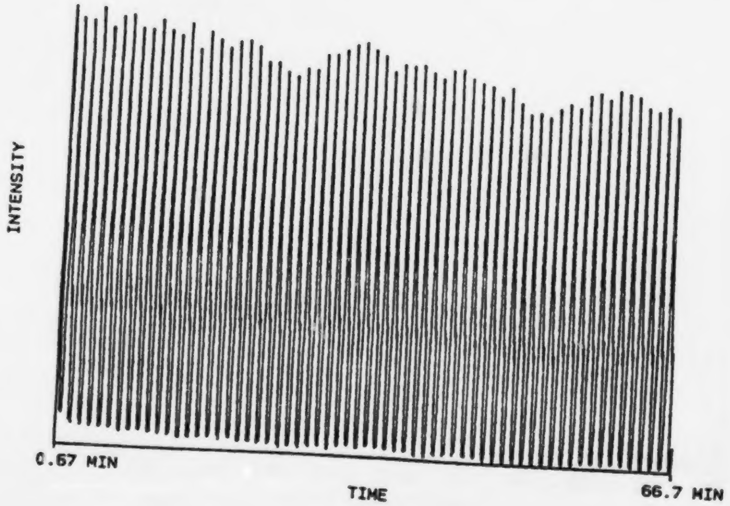


FIGURE 8. THE SERS SIGNAL FROM THE FOSP OF THE 1006 cm^{-1} PEAK OF PYRIDINE AS A FUNCTION OF OXIDATION/REDUCTION CYCLING (ORC).

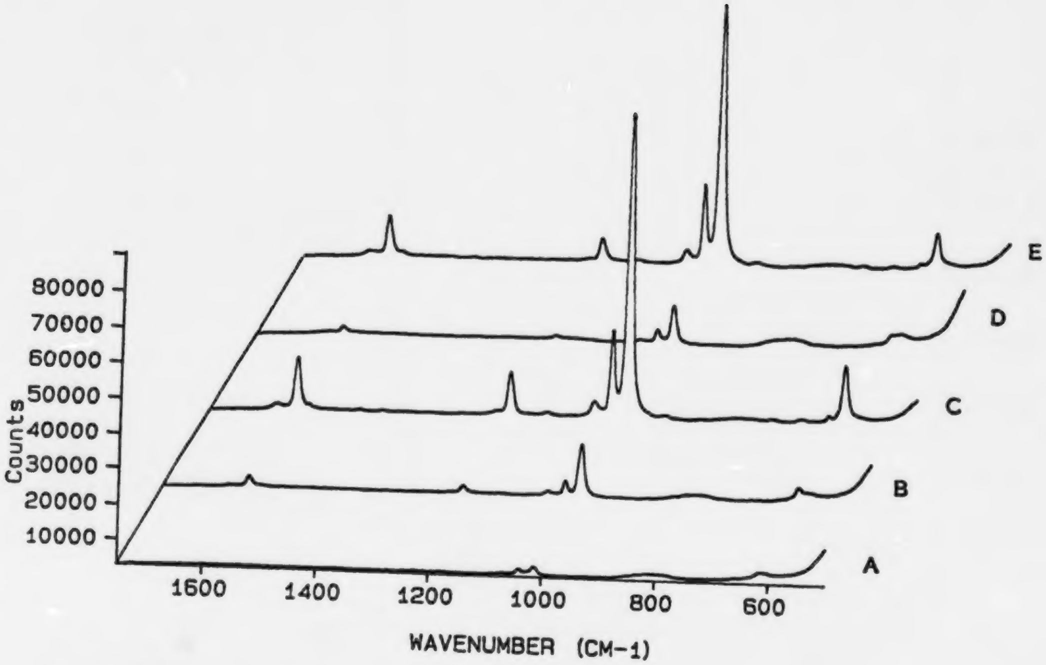


FIGURE 9. THE SERS SPECTRA OF 0.05M PYRIDINE AT 625 nm (100 mW).

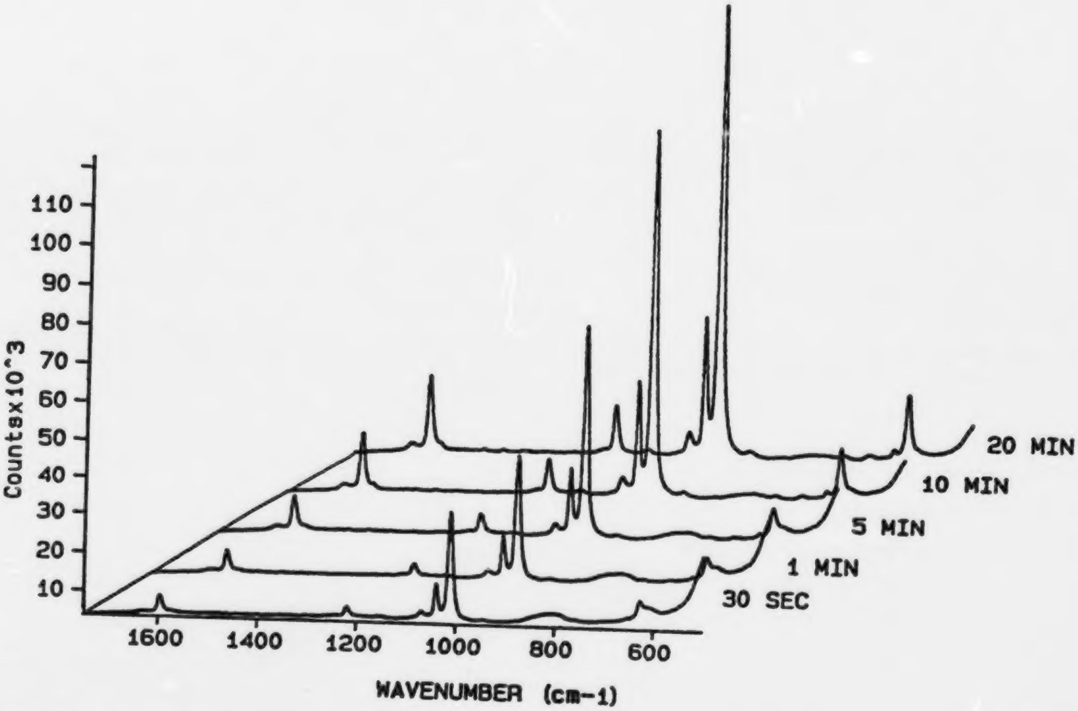


FIGURE 10. PREROUGHENED Ag ELECTRODE AT -0.7 in 0.02M PYRIDINE AFTER BEING HELD AT +0.2V FOR VARIOUS TIMES.

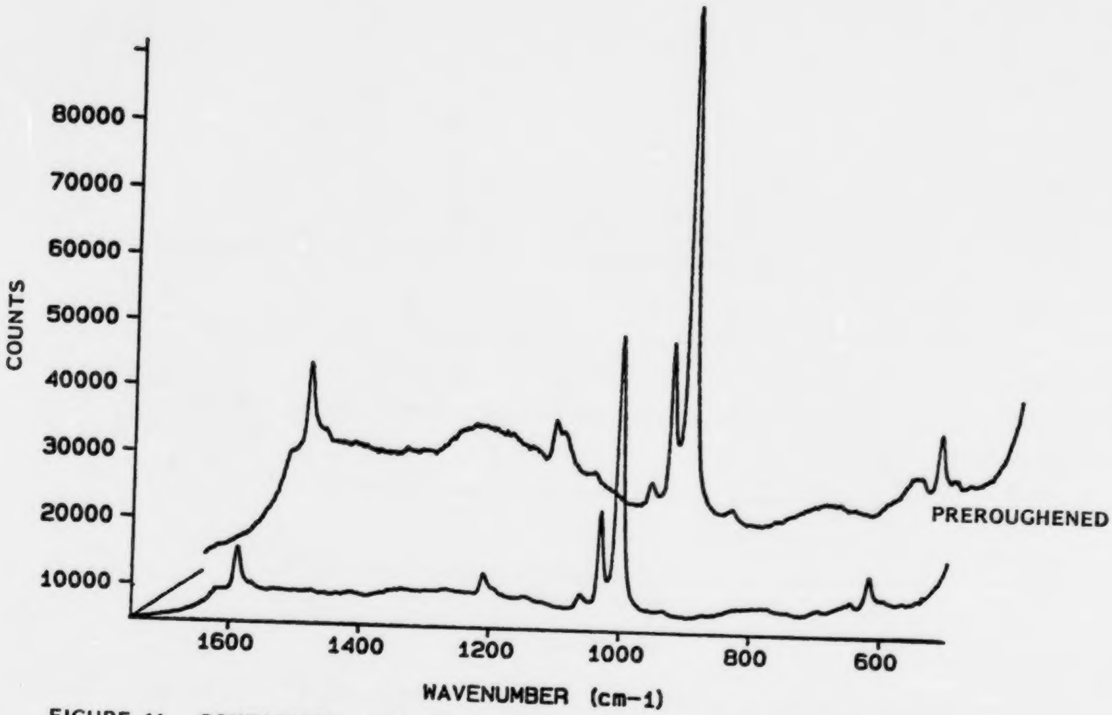


FIGURE 11. COMPARISON OF A POLISHED AND A PREROUGHENED ELECTRODE. SERS SPECTRA OF 0.02M PYRIDINE IN TAP WATER AT 625 nm AT-0.7V.

DISCUSSION

JOHN SCALERA: Using the potential of the electrode as one of your parameters to define the species in real sample situations, what difficulties do you have with poisoning of the electrode surface and throwing the potentials totally off?

Are you still able to pick up your species on the surface, even though it's poisoned and the potentials have shifted? By poisoning, I don't necessarily mean dramatic, but just throwing the potentials off so that you know it's uncharacteristic of what you're looking for.

MICHAEL CARRABBA: Yes, that may be a problem. We are in the process now of doing real-life samples in the laboratory, and that will be a question we will address in the future.

CHARLES MANN: You mentioned that the silica signals in the fiber optics change with time. What's the nature of the change and its origin?

MICHAEL CARRABBA: I wasn't talking about the fiber optics, the Raman band itself, changing with time. What changes is the electrode substrate, which will change the reflectants back into your collection system. If you can prevent it from getting into your collection system, it's not going to be a problem. The substrate will vary as an electrode potential, and it may roughen a little bit differently, from one time to the next.

With all these oxidation/reduction cycles, we observe a difference of about five percent in the signal intensities, which is pretty good for environmental applications.

FIBER-OPTIC SURFACE-ENHANCED RAMAN SYSTEM
FOR FIELD SCREENING OF HAZARDOUS COMPOUNDS*

T. L. Ferrell   E. T. Arakawa   R. B. Gammage   D. R. James
J. P. Goudonnet   R. C. Reddick   J. W. Haas   E. A. Wachter
Health and Safety Research Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6123

ABSTRACT

Surface-enhanced Raman scattering permits identification of compounds adsorbed onto a metal microbase that is microlithographically produced with submicron resolution. Less than one percent of a monolayer of a Raman active target compound offers a high signal-to-noise ratio. By depositing the microbase on the exterior of a fiber optic cable, convenient field screening or monitoring is permitted.

By using highly effective microbases, it is possible to reduce laser power requirements sufficiently to allow an economical, but complete, system to be housed in a suitcase. We shall present details of a SERS system of this type and shall show data on samples of interest in the screening of hazardous compounds.

Key words: Raman scattering, hazardous compounds

INTRODUCTION

There is a need for rapid and reliable on-site qualitative analysis of aqueous samples taken from aquifers, toxic waste sites, industrial and agricultural areas, and other environmentally sensitive locations. For many targeted compounds, the adsorption isotherm permits collection on a surface with suitable filters. Analysis of the spectra of the compounds, including deconvolution analysis for complex mixtures, can be carried out for a variety of methods that are sensitive to ultralow levels. Reliability of the analysis is affected by sample degradation for the relatively slower analytical techniques, and the aqueous samples pose limits for some methods such as infrared absorption spectroscopy. Surface-enhanced Raman spectroscopy (SERS) is a relatively new tool for analytical chemistry which fills a gap in the methods of attack available for detection of concentrations of parts per billion.

Raman spectroscopy identifies molecules by their vibrational and rotational spectrum, as does infrared absorption spectroscopy. However, in Raman spectroscopy one uses visible light, the Raman spectra appearing as wavelength shifts from the wavelength of the incident light. This requires that the incident wavelength be taken out of the scattered light by filtering or dispersion. Due to the fact that only a small fraction of the light is Raman shifted, one needs good filters or a double monochromator or an optimized combination. SERS provides signals comparable to those obtained in Raman scattering from solutions, but detects a factor of over one million less in the number of molecules. For instance, one reason for this is that silver microstructures (upon which the molecules are adsorbed) actually concentrate the electric field of the incident light. Since the scattering is proportional to the square of the field, this produces a scattering cross section that is adequately large. The high reflectivity of silver and the size and shape of the microstructures are important in optimizing the signal. We have produced several different types of microstructures using methods common to the semiconductor industry. Our results demonstrate a high performance level for silver microneedles evaporated at near grazing incidence onto an evaporated calcium fluoride surface. Electron micrographs and optical absorbance data have been taken in modeling our samples. Good agreement has been obtained with electrodynamical calculations which model the silver microneedles as prolate spheroids.

EXPERIMENTAL FEATURES

For on-site measurements it would be desirable to utilize fiber optic cables that can be used as extended probes or left over a period of time for monitoring purposes. We have demonstrated that SERS can be carried out using a totally internally reflected laser beam and have deposited several different types of microstructures on a prism base and on optical fibers. It now seems desirable to attempt to perform stimulated SERS by increasing the power density through improvement of the microstructures and use of higher power lasers. The data we have obtained to date using internal reflection show an adequate signal-to-noise ratio, but further investigation is warranted.

Due to the importance of the shapes of the microstructures, we have carried out exhaustive analysis of the geometries available for practicable systems. We have employed scanning-tunneling electron microscopy to obtain shape-effect data.

We have examined a number of compounds to test the performance of SERS. While it is more difficult to detect many of the more symmetric molecules--and in certain cases fluorescence contributes to the noise--a wide range of compounds of interest have demonstrated adequately large SERS cross-sections. Reproducibility problems have been encountered which need further research.

SUMMARY

SERS can be utilized in a convenient, rapid, and reliable form for a variety of on-site applications involving ultralow levels of targeted compounds. Some degree of development remains to be carried out in order to provide better reproducibility.

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*Research sponsored by Div. of Facility & Site Decommissioning Projects, USDOE, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

DISCUSSION

JOSEPH ANDRADE: Can you compare the enhancement factors you get with all the various geometries you suggested? I'm particularly curious about the silver post geometry, as opposed to the roughened electrode, which was discussed by your colleague.

Second, regarding surface chemistry aspects: if I remember right, the enhancement field drops off over about ten angstroms. What are you doing on the surface of the silver to minimize water vapor absorption, for example, and to treat the surface in such a way that you get the enhancement, but still minimize some of the nonspecificity which will obviously be present?

ERIC WACHTER: To answer the first question, one area of tremendous importance is to decouple the chemical effects from the physical effects. I think of the electrode as a celebration of chemical effects, where we're putting a lot of the physical emphasis for the SERS effect on preferentially absorbing material.

With the substrate materials, without the application of the electrochemical approach, we're looking primarily at the effects of the electromagnetic enhancement.

I don't think it's possible to directly compare the results from the electrochemical approach to the post spheres.

For the electrode approach, the surface is relatively uncontrolled, in terms the microscopic topography.

MICHAEL CARRABBA: Once made, it's very controllable and reproducible to obtain the same surface over the oxidation/reduction cycle.

We can't controllably make a substrate with, say, ten angstroms, *A* to *B* ratio; but once we have a surface, we can calibrate it.

The best enhancements that we have obtained on the electrodes are around 10^5. We might be able to do a little better if we had some controlled electrode substrates. These have been under discussion between EIC and Oak Ridge National Labs.

ERIC WACHTER: We need to develop the electrode approach, with some sort of a tailored surface, so we can combine both phenomena to result in the highest enhancement.

GREG GILLISPE: What will be the laser for a field unit? Dr. Carrabba showed that being able to choose the wave length to launch the surface plasma is very important, and of course the effect is directly proportional to the laser power. The more laser power in, the more signal you're going to get, subject to some background limitations. What are your thoughts on what the ultimate laser in a field unit might be?

MICHAEL CARRABBA: We hope to have a prototype system to do some field measurement sometime in mid-February 1989. The advancements in microlaser technology have been fast and furious, and there are research scale lasers available that will give you about 100 milliwatts of intensity at 532 nanometers. Those are diode pump YAGs.

One hundred milliwatts is more than necessary for this technique. Most of these slides that I showed were done at about 100 milliwatts of laser intensity, and there have been reports from Oak Ridge of 0.7 milliwatts of intensity.

I believe that the laser of choice will be a diode pump YAG, which will have frequency doubling capabilities. It will give you multi-dimensional capabilities, because you can use the 532 nanometer wavelength for silver, and hopefully you could use the diode at 680 for copper and gold surfaces.

There has also been work reported by Mike Angel and Bruce Chase of doing SERS at 1064. There seems to be a large enhancement at 1064, so that's another wavelength of choice.

Those are three optimum wavelengths with a diode pump YAG system, and that's the system that we are trying to acquire for our portable instrument.

GREG GILLISPE: You showed spectra with a dramatic difference between the 575 and 620 excitation. Is that something that can be overcome?

MICHAEL CARRABBA: That's part of the selectivity of the technique, because with silver, you want to use the 575, and on copper, you want to use the red wavelength.

Copper gets even better towards 700 nanometers, as does gold. So there is that advantage to using that diode pump system – taking some of the diode light and using that for your analysis.

ERIC WACHTER: I think the results you're discussing are perhaps a little bit deceptive. What one can show is that there will be an optimum wavelength for a particular substrate material. And if we want to use both silver and copper for their various chemical and absorption effects, then for optimal SERS enhancement, we're probably constrained to using two different wavelengths.

GREG GILLISPE: But having 532 and 680 would be sufficient? Do you really sacrifice very little flexibility that way?

MICHAEL CARRABBA: We could use 514 for silver, with no difficulty at all. 532 is better than the argon wavelength and a little bit less than 575, but the trade off is not that much.

POROUS FIBER OPTIC FOR CHEMICAL SENSORS

M.R. SHAHRIARI, Q. ZHOU, G.H. SIGEL, JR.
RUTGERS UNIVERSITY, FIBER OPTIC MATERIALS RESEARCH PROGRAM, PISCATAWAY, NEW JERSEY

GRANT STOKES
GEO-CENTERS, INC., NEWTON CENTRE, MA 02159

ABSTRACT

A novel fiber optic sensor has been developed for in line monitoring of chemical species in gas and liquid systems. The sensor is based on a porous optical fiber device developed at the Fiber Optic Materials Research Program, Rutgers University. In this approach, a small region of a fiber (~0.5 cm) is made porous and a chemical reagent is immobilized in the pores. The porous section is an integral part of the fiber. The preliminary experimental results for detecting ammonia and moisture in the gaseous state and pH in the liquid state suggest excellent sensitivity, reproducibility and a wide dynamic range. These results also suggest the feasibility of developing a wide range of sensors for on-line monitoring of ground water contaminants at superfund sites using the porous glass fiber approach.

INTRODUCTION

The use of optical fibers as components of chemical sensors for in situ monitoring of different chemical species is a relatively recent development. In these sensors light propagating through the fiber interacts with a reagent that in turn specifically and selectively interacts with the environment to be sensed. The typical optical properties monitored include absorption, fluorescence or chemiluminescence. The reagents are normally immobilized a membrane or porous polymer matrix which is used to coat the fiber tip, or in the case of evanescent sensors, the fiber cladding. One of the problems encountered with the fiber optic chemical sensors based on evanescent absorption is the characteristic low sensitivity which is due to limited depth of penetration of evanescent light into the reagent cladding [1-4].

In this study, we describe a novel approach for developing a generic, reversible and high sensitivity chemical sensor based on porous glass fibers. Figure 1 illustrates the principle of detection for a porous glass fiber as compared with a conventional evanescent sensor. In a typical evanescent fiber optic sensor, the sensitivity is limited both by the depth of penetration of evanescent light into the reagent coated on the fiber core as well as the number of internal reflections. In a porous fiber, the analyte penetrates into the pores and interacts with the reagent which is previously cast into the pores. Since the porous fiber has large surface area, absorption is enhanced dramatically, leading to the high sensitivity of the sensor. Another interesting advantage of a porous glass fiber is the elimination of problems associated with the physical and optical coupling of the sensor probe to the fiber due to the very small sensing region (about 0.5 cm in length and 250 microns in diameter) which is an integral part of the fiber waveguide. In addition, multiple fiber sensors can be deployed from a single analytical unit and are expected to be less expensive than conventional sensors based on materials cost and ease of fabrication.

FABRICATION OF POROUS GLASS FIBERS

The material used in the porous fiber is an alkali borosilicate glass with the composition of 60% SiO_2, 30% B_2O_3 and 10 (wt.%) alkali oxides. This type of glass is chosen as it is a well characterized system, producible at a low cost, and most importantly, it exhibits the phenomena of liquid/liquid immiscibility within a certain temperature range. The above composition is melted in an electrical furnace at 1400°C and cast into rods with a 20mm diameter and 0.5m in length. The rods are then drawn into fibers at approximately 700°C by a draw tower equipped with an electrical furnace. Fibers with a 250-300 micron diameter and many meters long are produced in this manner. Fiber are broken into strands of 5 cm to 10 cm in length. A portion of fiber (about 0.5 cm) is heat treated in a tube furnace at 600°C for about 3 hours. At this point, the heat treated glass is phase separated into a silica rich phase and a boron rich phase. The boron rich phase is leached from the glass by placing the fiber in a bath of 1 normal hydrochloric acid at 95°C for 3 hours. The fibers are subsequently washed with distilled water and rinsed with pure alcohol. Figure 2 shows the flow diagram of the processing steps for producing porous fibers.

CHEMICAL TREATMENT

Once the fiber is prepared, the porous segment is cast with the sensing reagent (indicator). This is accomplished by dissolving the reagent in a solvent at a predetermined concentration and soaking the porous fiber in the solution. The reagent then is dried into the pores by heating the fiber. The colorimetric indicator used for ammonia gas sensor was bromocresol purple (Fischer Scientific Co. B. 393). Bromocresol purple is generally stable at room temperature and is resistant to photochemical degradation upon exposure to visible light. When the indicator is exposed to ammonia gas a significant absorption peak develops at 580 nm. Cobalt chloride ($CoCl_2$) was the reagent used for the humidity sensor. In the presence of moisture $CoCl_2$ can form a hydrated salt having 6 molecules of bound water. When it is well dried, it appears bright blue and has high optical absorption between 550 - 750 nm. When it is hydrated it appears pink and the absorption peak shifts to 500 nm. Bromocresol green and bromocresol purple were used in the pH sensor. In this latter sensor, the reagents were immobilized onto the pores by activating the surface of the glass by silanization techniques and coupling the reagents to the activated glass surface.

RESULTS AND DISCUSSION

Using BET and mercury porosimeter analysis, micropores and macropores within the porous fiber were investigated respectively. The distribution of the pore size from BET is as follows:

Pore Diameter	Pore Volume
> 80 Å	3.0×10^{-2} ml/g
10-20 Å	14.2×10^{-2} ml/g

The pore size results from the mercury porosimeter is as follows:

80-400 Å	2.4×10^{-2} ml/g

The BET results indicate that surface area of pores is about 200 (m^2/g). Figure 3 shows the SEM micrographs of cross sections of the porous fibers before and after phase separation and leaching. The micrograph (3C) shows clearly that the fibers have a structure with interconnective porosity.

The preliminary experimental results for porous glass fibers used as humidity and ammonia gas sensors indicate excellent sensitivity, reversibility, and reproducibility. The response curves for ammonia gas and humidity are shown in Figures 4 and 5, respectively. The calibration curves for ammonia gas, humidity and pH sensors are shown in Figure 6.

SUMMARY

In summary, a new class of porous glass fiber optic chemical sensor has been demonstrated. Gases or liquids permeating into a suitably pretreated, porous fiber optic core are detected by in-line optical absorption. Although this paper focuses on the monitoring of certain chemical species and pH, the basic design principles of the device are applicable to the monitoring of a wide range of liquids and gasses with ground water contaminants and biomedical sensors among the promising candidates for future studies.

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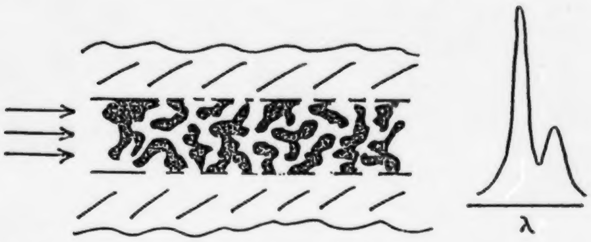
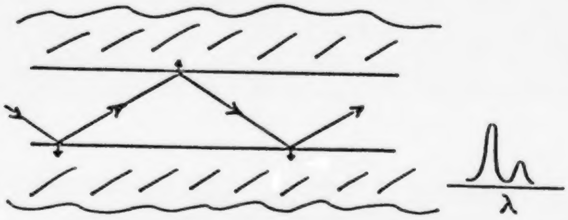


a) Porous configuration creates large surface areas for maximum absorption



b) Light penetration and hence absorption is limited in evanescent configuration

FIGURE 1

Principle of detection for porous glass chemical sensor (a) as compared with typical evanescent sensor (b). The porous glass sensor achieves high sensitivity over a very short sensing region.

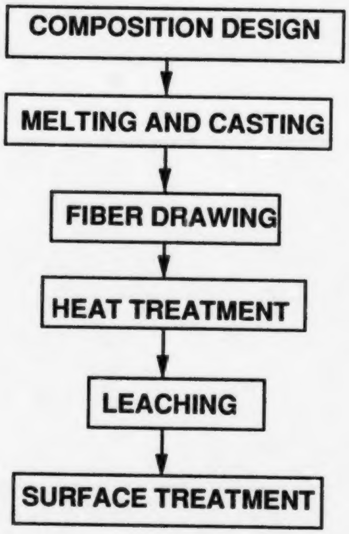
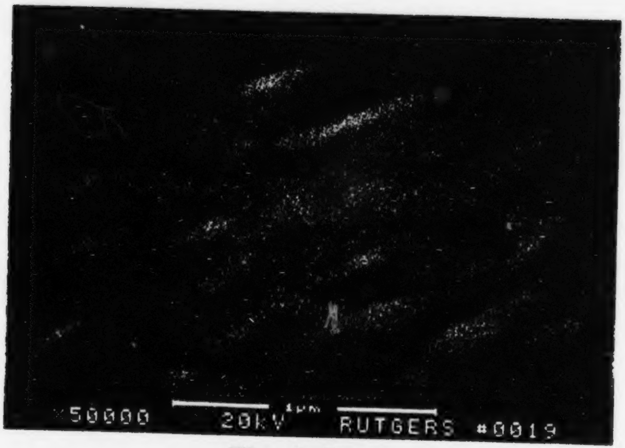

COMPOSITION DESIGN
MELTING AND CASTING
FIBER DRAWING
HEAT TREATMENT
LEACHING
SURFACE TREATMENT

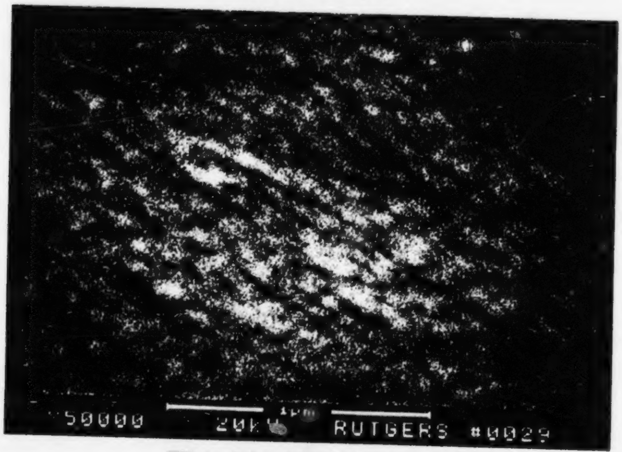
FIGURE 2

Processing Steps for Producing Porous Glass Fibers

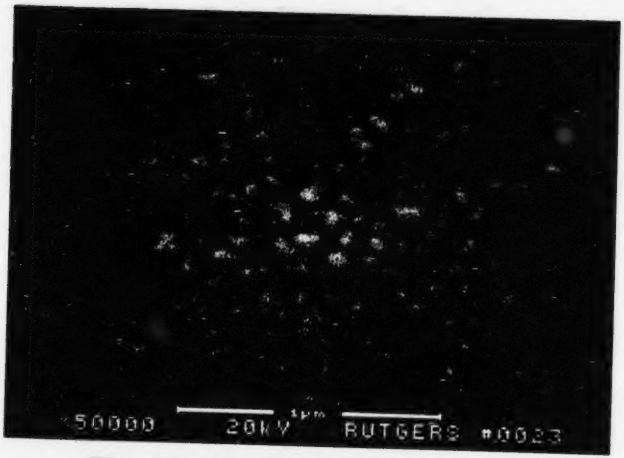
Reproduced from
best available copy.


50000
20kV
1µm
RUTGERS #0019

Fiber As Drawn
FIGURE 3A


50000
20kV
1µm
RUTGERS #0029

Fiber After Heat Treatment
FIGURE 3B


50000
20kV
1µm
RUTGERS #0023

Fiber After Heat Treatment And Leaching
FIGURE 3C

SEM MICROGRAPHS OF CROSS SECTION OF A FRACTURED FIBER

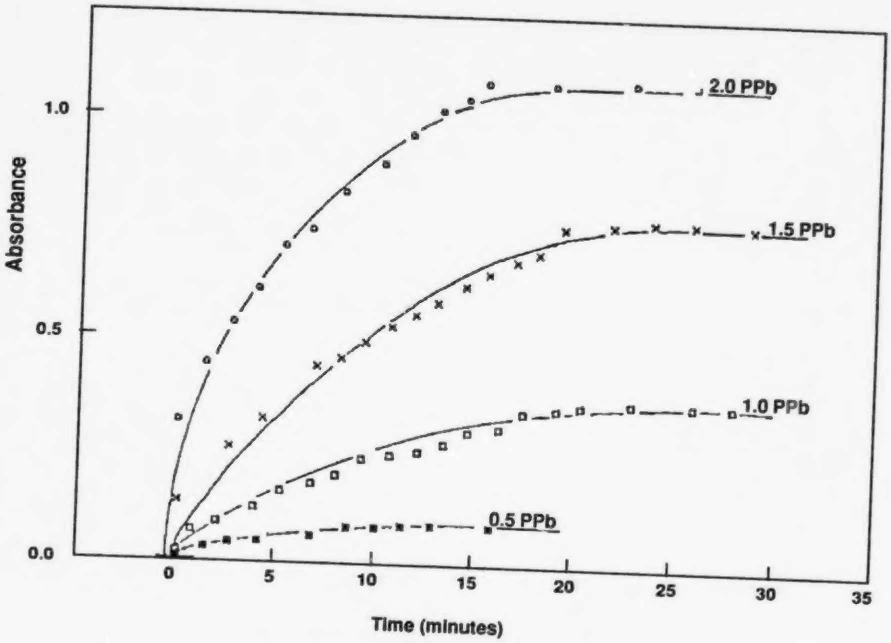


FIGURE 4
Response Curve for Porous Glass Ammonia Sensor at Different Ammonia Concentrations.

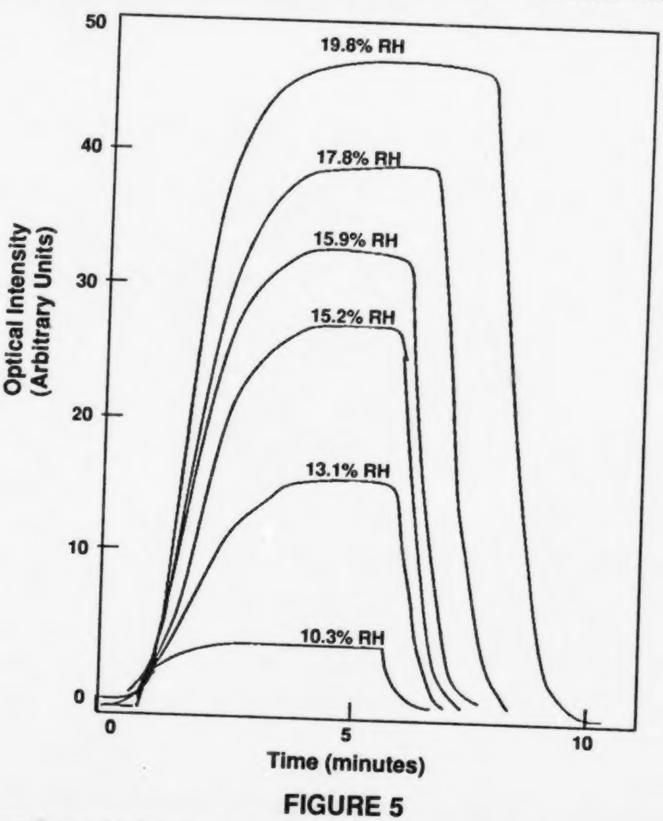


FIGURE 5
Response Curve for Porous Glass Humidity Sensor at Different Humidity Levels.

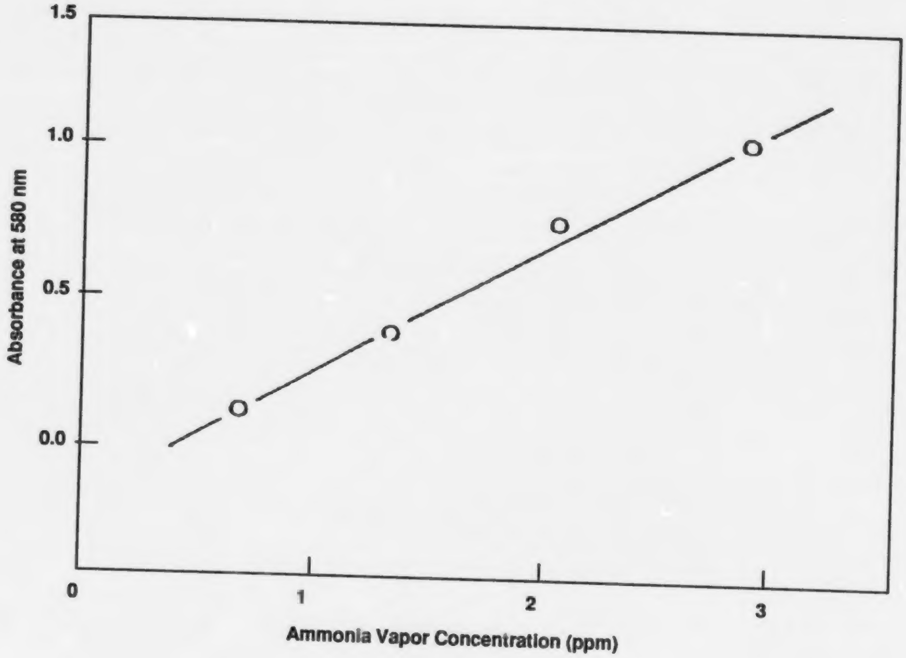


FIGURE 6A

Calibration Curve for Ammonia Gas Sensor Based on Porous Glass Fiber.

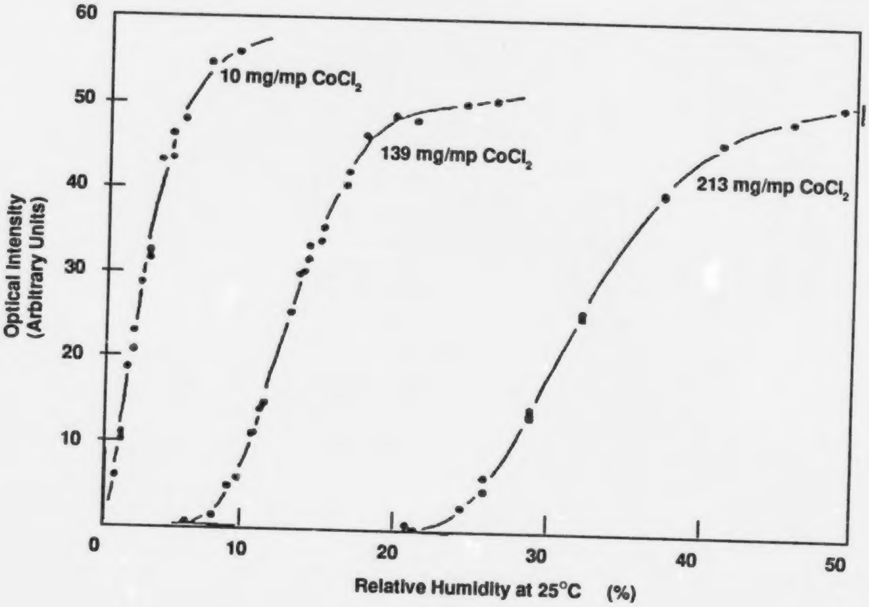


FIGURE 6B

Calibration Curves of Relative Humidity Sensor Based on Porous Glass Fiber Treated with Different $CoCl_2$ Concentrations.

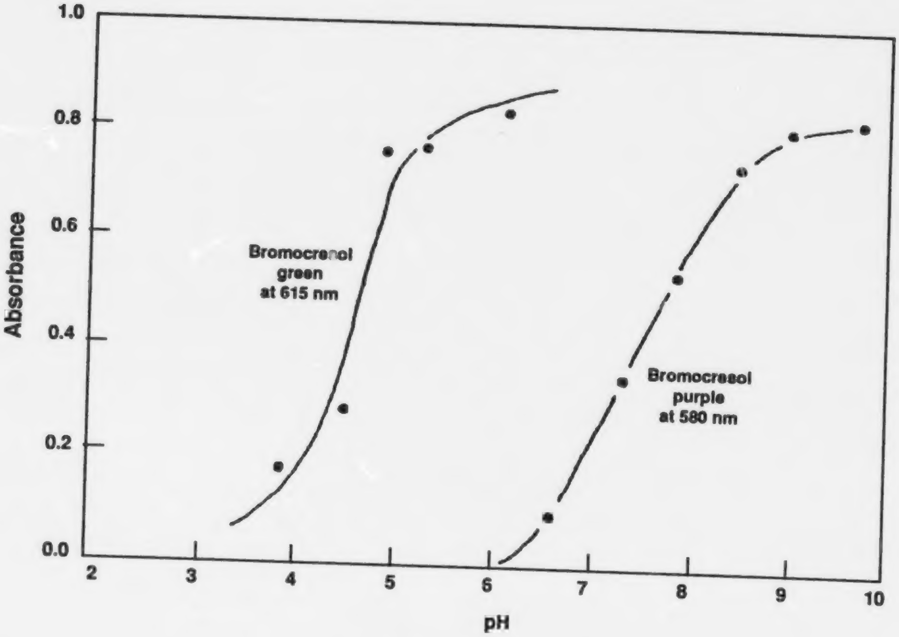


FIGURE 6C

Calibration Curves for pH Sensor Based on Porous Glass Fiber with Immobilized Inidcators.

DISCUSSION

STEVEN SIMON: What pore size is on there?

MAHMOUD SHAHRIARI: We can control the pore size, depending on what we want to sense, what kind of indicators we want to put there, and what the molecular size of the indicator is. Regarding limitations, the smallest pore is about 10 to 20 angstroms, and the largest is about 800 angstroms.

STEVEN SIMON: What if you went into a real-world environment? For example, have you tried the pH sensor, particularly, or anything other than laboratory standards? My concern would be clogging of the sensor.

MAHMOUD SHAHRIARI: Yes, clogging is obviously one serious problem to be considered.

STEVEN SIMON: When you make the tip, it's part of the fiber optic cable. What would you do in the case of nonreversible systems, or probes versus a reversible sensor?

MAHMOUD SHAHRIARI: So far, we have only been considering the reversible sensors, not the probes. So for humidity, ammonia gas, pH, and for future applications, we would like to use reversible indicators, rather than irreversible.

STEVEN SIMON: You're looking mostly at absorption base systems. Have you calculated based on the fluoropher approximately what kind of sensitivity you could get for something like ammonia?

MAHMOUD SHAHRIARI: Yes, we are currently working on a fluorescence sensor for carbon monoxide and carbon dioxide sensors. Those are reversible.

CHARLES MANN: Given the effectiveness of the electrochemical pH measurement, what is the advantage of the type of pH sensors that you are suggesting? An electronic sensor would presumably have as great a physical range as the fiber optic one, wouldn't it? It seems that the pH electrode does essentially the same thing, and I was inviting some instruction as to why the fiber optic system is superior.

MAHMOUD SHAHRIARI: I would say that the advantages of fiber optic systems over electronic sensors include electromagnetic immunities, small size, cost, and the like.

IMPROVED LUMINESCENCE TECHNIQUE FOR SCREENING AROMATIC CONTAMINANTS IN ENVIRONMENTAL SAMPLES

R. B. Gammage J. W. Haas, III
G. H. Miller T. Vo-Dinh
Oak Ridge National Laboratory
Health and Safety Research Division
P. O. Box 2008
Building 7509, Mail Stop 6383
Oak Ridge, Tennessee 37831-6383

ABSTRACT

The sensitive spectroscopic technique of synchronous fluorescence (SF) is readily applied to screening environmental samples for semi-volatile aromatic contaminants. The technique is applicable to water and soil samples, either directly as water or as solvent extracts. This screening technique permits identification of semivolatile EPA priority pollutants or groups of pollutants, such as polynuclear aromatic (PNA) hydrocarbons of common ring size, in key environmental samples. Conversely, negligibly contaminated samples requiring no further analyses and expense can be screened out. Examples are given of coarse but direct screening analyses of contaminated samples of groundwater. The total synchronously measured fluorescence has been expressed in units of total PNA referenced to the SF from a standard reference sample of sixteen PNA compounds.

INTRODUCTION

Very large numbers of samples from hazardous waste sites are being collected and analyzed by conventional methods to characterize near-surface and subsurface contamination. Analyses for some categories of organic pollutants, such as semivolatile organics, are expensive, often costing several hundred dollars for a single class of compounds (1). The cost typically exceeds $2,000 for the full battery of semivolatile, PCB/pesticides and volatile organic compounds.

Because current procedures for conducting environmental surveying and monitoring are extremely costly and time-consuming, alternate or adjunct rapid screening procedures are very attractive. For example, chemical screening tests, preferably ones having the sensitivity of prescribed EPA standard procedures, can be used to inexpensively identify uncontaminated samples requiring only limited or no further action and expense. In addition, one can cost-effectively identify samples with significant levels of specific compounds or groups of pollutants. One is then able to devote more definitive and costly analytical procedures only to samples deserving such attention and expense. Screening heavily contaminated samples is also valuable in preventing excessive levels of organics from entering a GC/MS instrument such that down time of hours or days are required to return the instrument to a clean operating condition.

A relatively simple method exists that allows large numbers of samples to be analyzed for volatile organics in a relatively short period of time. This is the EPA Method 5020 or Headspace Method. There is no analogous method available for screening samples containing semivolatile organic contaminants. The need for new techniques suited for field screening of semivolatile organic contaminants was highlighted recently in a guidance document for fundamental research in subsoils and groundwater (2).

In this paper we describe a candidate method for screening environmental samples that contain luminescing semivolatile aromatic contaminants; this spectroscopic technique is based on synchronous fluorescence (SF) (3) with sensitivity capable of detecting ppb concentrations of strongly fluorescing compounds.

SPECTROSCOPIC TECHNIQUE

The use of luminescence techniques to analyze complex environmental samples is often limited in spite of inherently excellent sensitivity. The problem is usually caused by spectral overlap due to large numbers of luminescing compounds in real-life samples. Our aim for screening

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is to make improvements in analytical selectivity without seriously compromising simplicity in experimental protocol or sensitivity.

Synchronous Fluorescence (SF)

In synchronous excitation spectroscopy (4), the luminescence signal is recorded while both emission and excitation monochromators are scanned simultaneously. The wavelength interval, Δλ, between the two monochromators is kept constant throughout the measurement. The spectra of the individual components are simplified and the bandwidth narrowed. We are applying the concept most often in SF because of its direct application to the analysis of liquid samples such as groundwater.

When dealing with a single fluorescing compound, the optimum value of Δλ for spectral simplification is determined by the Stokes shift, i.e., the wavelength difference between the 0-0 bands in emission and absorption.

In the case of a sample containing a complex mixture of fluorescing PNA, we often find that the optimal selectivity and sensitivity are attained when Δλ is set at 3 to 5 nm.

The concept of synchronous excitation can also be used with room temperature phosphorimetry (RTP) (5,6). The optimum value of Δλ is the singlet-triplet energy difference of the compound, which is usually between 150 and 250 nm. The RTP technique can be used to provide screening information complementary to that obtained by SF. The particular groundwater samples discussed in this paper produced only barely measurable RTP. Consequently the RTP screening technique will not be discussed further. Readers interested in RTP applied successfully to the screening of environmental samples are referred to reference 3.

APPLICATIONS

Preliminary tests have been performed on groundwater taken from wells at the Bear Creek burial grounds located on the Department of Energy reservation at Oak Ridge, Tennessee. The hazardous organic waste is composed principally of degreasing solvents and transformer and machine oils. Anthropogenic luminescing constituents are associated with these waste oils.

Synchronous Fluorescence of a Standard Reference Sample

The SF was determined for a National Bureau of Standards (NBS) reference sample of 16 PNA (NBS SRM 1647). The PNA-containing solution of acetonitrile was added to water to give dilutions of 1:100, 1:200, 1:600, 1:1000 and 1:3000. At least three SF measurements were made at each concentration. The SF intensity was measured and integrated in steps of 1 nm over the wavelength range of 240-560 nm. Blanks were also run and their integrated SF subtracted in order to produce the 5-point calibration curve shown in Figure 1.

Synchronous Fluorescence of Polluted Well Waters

Withdrawn samples of well water were stored in a refrigerator. Prior to the SF screening, the water samples were passed through a 0.45 μm membrane filter to remove particulate matter. The selectivity of the SF technique is demonstrated in Figure 2. Individual compounds have not been identified. However, 2- and 3-ring PNA generally fluoresce at 300-400 nm while 4- to 6-ring PNA fluoresce at 400-600 nm. Samples can thus be coarsely categorized according to ring size using SF screening.

These same samples were ranked by measuring and integrating the SF intensities at selected wavelengths and comparing the integrated SF to that from the reference sample of PNA. In this manner the SF from the well water samples shown in Figure 2 have been converted into PNA equivalent units of the NBS reference sample.

This type of direct measurement on water samples is easy to make but gives only limited qualitative information. One drawback is that PNA bound to particulate matter were removed in the filtration clean-up step and, therefore, missed in the SF measurement. A better and only slightly more complex screening measurement might be to enhance the PNA solubility by addition of a water-miscible solvent such as ethanol. Another problem is fluorescence from naturally occurring compounds such as those produced by decaying vegetable matter (7). Future studies will need to address the problem of discrimination between natural and anthropogenic fluorescing compounds.

SF screening has also been used to monitor temporal changes in the fluorescing compounds of several well waters. In the instance of two groundwater samples collected from well GW 39 six months apart, Figure 3, the nature of the fluorescing constituents remained unchanged. Referenced to the NBS standard, the PNA in the wellwater were equivalent to between 1 ppm and 2 ppm.

At the time that well GW 39 was drilled, the core soil samples were analyzed by EPA reference methods and found to be free of any PNA contaminant. There is, however, a nearby oil-retention pond. It is conceivable that the traces of fluorescing material we are detecting have as their source the contaminated pond water. An example of a fluorescing component newly appearing in ground water is shown in Figure 4. For well GW 15 the new constituent fluorescing at about 500 nm has an equivalent concentration of 5 ppm. Examination of Figure 5 suggests that the same fluorescing compound might also have appeared recently in GW 23. Otherwise, the SF spectrum for well water GW 23 has remained qualitatively little changed over a period of two years.

SUMMARY

The technique of SF has a previously demonstrated utility for enhancing selectivity in the analysis of environmentally-related samples containing luminescing organic contaminants. Preliminary testing indicates that this same technique can be applied to the measurement and screening of groundwater contaminated with luminescing semivolatile organic compounds. Measurement of the SF gives an indication of the dissolved PNA content in a groundwater sample. A coarse ranking of a series of groundwater samples can, therefore, be made according to their PNA content. A semi-quantitative estimate of the total PNA content of several groundwater samples was made by reference to the SF from an NBS standard of sixteen PNA compounds.

Qualitative differences in the composition of fluorescing constituents could be discerned quite readily. This property permits one to monitor groundwater periodically and detect the appearance or disappearance of specific entities.

ACKNOWLEDGMENTS

Research sponsored by the U. S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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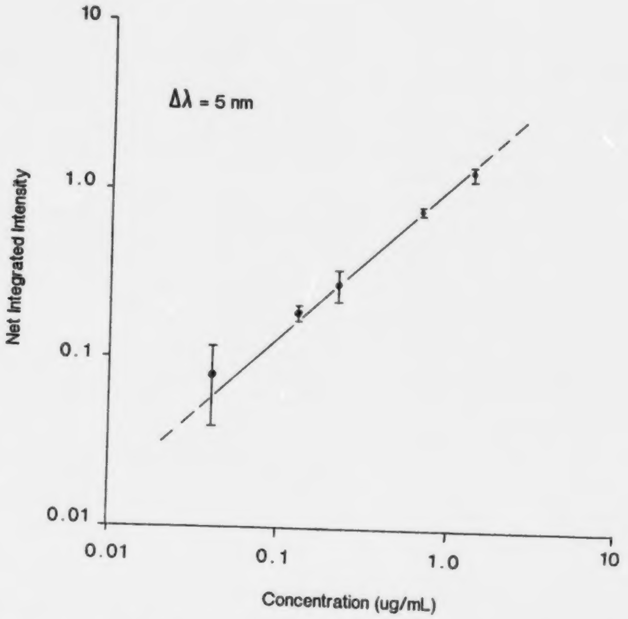

FIGURE 1 CALIBRATION CURVE OF SF INTENSITY FOR A NATIONAL BUREAU OF STANDARDS REFERENCE SAMPLE OF 16 PNA COMPOUNDS

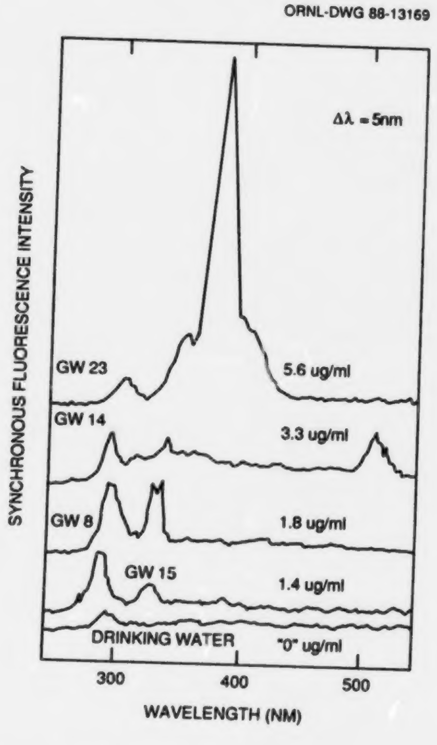

FIGURE 2 SYNCHRONOUS FLUORESCENCE FROM POLLUTED GROUNDWATER SAMPLES REFERENCED TO A 16 COMPONENT MIXTURE OF POLYCYCLIC AROMATIC HYDROCARBONS

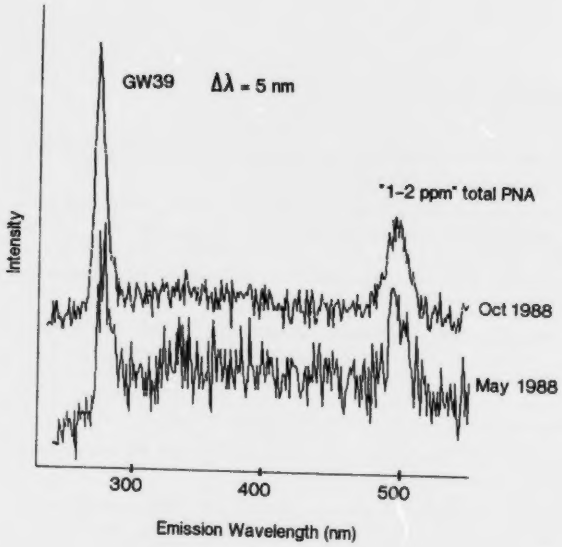

FIGURE 3 EXAMPLE OF WELL WATER IN WHICH TRACES OF FLUORESCING MATERIAL REMAIN RELATIVELY UNCHANGED OVER FIVE MONTHS

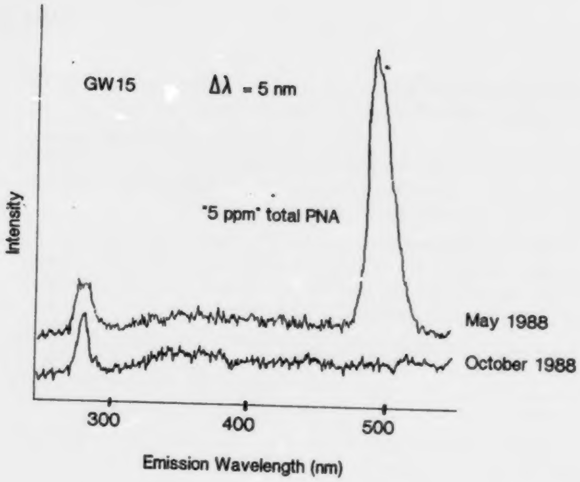

FIGURE 4 EXAMPLE OF NEW FLUORESCING MATERIAL APPEARING IN WELL WATER OVER A FIVE-MONTH PERIOD

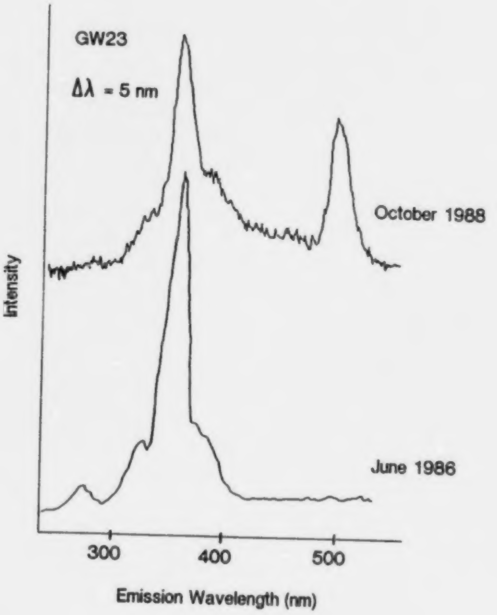

FIGURE 5 QUALITATIVE CHANGES IN THE SYNCHRONOUS FLUORESCENCE SPECTRA OF A WELL WATER AFTER TWO YEARS

DISCUSSION

MARTIN VANDERLAAN: I'm having a little trouble with the idea of large polynuclear aromatic hydrocarbons being in water.

Are these on suspended particulates in the water, and what do suspended particulates do to your NBS standard? Do you get self quenching, or anything like that if it is on particulates? Are you really measuring filtered water, or are you measuring the particulate phase?

RICHARD GAMMAGE: In the case of the NBS sample, it comes in a solvent, and we take a little bit of it and dissolve it in pure water. That calibration curve is for pure material, dissolved in water at low concentrations, where we're not getting any saturation and precipitation.

When we go to the field samples, we're taking the well water, as is, and making measurements. So if there are problems with material being on colloidal particles, as opposed to being in true solution, we're measuring the gross effect of those two. We haven't done any work yet to distinguish between the two.

MARTIN VANDERLAAN: I don't have any trouble if you rank order samples. I do have trouble if you compare to a standard curve, which is in something that really isn't the same matrix that you're measuring. You just said you didn't correct for things like pH, and we know pH is going to influence fluorescence. Other things like that have to be controlled.

RICHARD GAMMAGE: You're absolutely right, and it's really just a scrude screening technique at the moment.

TUAN VO-DINH: In fact, the polyaromatic hydrocarbons, the ones that have no heterocyclics are very insoluble in water. For benzoin, I think the solubility is about 10^{-6} molal. But what we did here is that in the standard, the trick is to dilute with ethanol. One-to-one ethanol increases the solubility tremendously, for one thing.

Secondly, what we measure in the well samples were filtered through. We don't know whether it's full of hydrocarbons, or metabolites, or the hydroxide of this compound. What we see here is a true screening. In fact, if you have a lot of polyaromatics, and you prepare samples, you have to be sure that you find a compatible solvent, and in that case we dilute in ethanol.

JOHN EVANS: What sort of apparatus are you using? Is this commercially available equipment, or is it home grown?

RICHARD GAMMAGE: We used commercially available equipment. A regular spectrofluorimeter, and the synchronous monochromate is now a standard option that one can buy. And even with the complicated instruments that we buy ($12,000-$15,000), I think one can take these sorts of measurements with a much cheaper model, probably down in the $5,000 range.

Detection of Solvent Vapors Using Piezoelectric Sensors

E.B. Overton
D.A. Gustowski, L.H. Grande,
H.P. Dharmasena, P. Klinkhachorn,
C.S. Milan and G.R. Newkome
Institute for Environmental Studies
Louisiana State University
Baton Rouge, Louisiana

ABSTRACT

The ability to separate and quantitate components in complex mixtures, such as air samples from the environment, is found mainly in intricate analytical instrumentation used in the laboratory. There arises the need for portable and reliable on site equipment for environmental testing. Such needs include responses to hazardous chemical spills, waste site cleanups and monitoring work areas for potential exposure to toxic chemicals. The methods employed in this instrument development project include development of rugged, field deployable instrumentation. Our approach in this case is to use neutral organic host complexing agents as coatings on quartz crystal microbalances (both bulk and surface acoustic wave type) to develop molecular size selective detectors for analysis of volatile substances.

INTRODUCTION

Piezoelectric quartz microbalances (PQM) and surface acoustic wave (SAW) devices have been of interest for the development of analytical vapor detectors. Since King (1) introduced the concept in the mid-sixties, chemists have used oscillating crystals as sensitive gravimetric detectors. When stimulated by an external electronic circuit, these crystals oscillate at a precise frequency due to the formation of dipole moments in the crystalline molecule. If any perturbation occurs at the surface of the crystal, in particular a change in mass, a corresponding change in the frequency of oscillation will occur. This relationship between frequency and mass change was first described by Sauerbrey (2) in the equation

$$\Delta F = 2.3 \times 10^{6} F^{2} (\Delta M / A) \qquad (1)$$

where: ΔF = change in frequency; F = fundamental resonance frequency of the crystal; A = area of the coated crystal; and ΔM = change in mass caused by sorption of vapors onto the coated crystal.

The high oscillation frequency of these crystals leads to extremely high mass sensitivity. 10MHz quartz crystals have approximately a 1 Hertz change in frequency for every nanogram adsorbed onto the crystal. The SAW vapor sensors are similar to the bulk wave piezoelectric quartz crystal sensors but have the advantage of substantially higher sensitivity. This is due to their higher operating frequencies (note that ΔF is proportional to the square of its fundamental frequency). For example, a 158MHz SAW device can provide resonant frequency shifts of about 400Hz for a one nanogram change in mass. Analytical applications are designed to use the high mass sensitivities of vibrating quartz crystal microbalances to detect low levels of volatile chemicals that can be sorbed onto the vibrating crystals' surface.

Though highly sensitive, the crystals are not selective since they respond to any change of mass at their surface. Based on polar interactions of molecules, coatings have been used to couple selectivity with the sensors sensitivity. Various coatings have been utilized to distinguish different solvent vapors using the piezoelectric quartz microbalance and the surface acoustic wave device. Stationary phases commonly used in chromatography, such as tenax and OV-1, have been used (1).

In the present study, host-guest complexation was investigated as a potential method for differentiation of solvent vapors for the PQM and SAW devices. Host-guest complexation occurs when a large organic molecule (the host) combines with a smaller solvent-type molecule (the guest). This phenomenon is known as inclusion. In general, the host molecules have two properties which enable them to form neutral complexes. These properties are a cavity of a specific size and shape, and the ability to establish some type of attractive force between the host and the guest which is reversible. For any molecule to become a guest, it must be precisely oriented to and of the same physical dimensions as the cavity in the host molecule.

The response of a liquid coated quartz crystal to various volatile solutes can be mathematically described by combining the Sauerbrey equation and the partition equation (3)

$$\Delta F = 2.3 \times 10^6 F^2 W_{liq} M_s / M_l \; P / P^\circ \; 1 / v \quad (2)$$

where: W_{liq} is the weight of the nonvolatile liquid; M_{liq} is its molecular weight; M_s is the molecular weight of the solute; P is the partial pressure of the solute vapors; P° is the vapor pressure of the solute at the temperature of adsorption and v is the activity coefficient.

Examination of this equation reveals that the frequency response of the crystals is proportional to the term P / P° and the reciprocal of v. If the solute is a relatively volatile substance, i.e. it has a high vapor pressure (P°) at ambient temperature, the term P / P° will be a small number. Consequently, the frequency response for detection of a volatile substance will be small. This factor limits the usefulness of quartz crystal microbalances to the analyses of relatively nonvolatile compounds, and of course, relatively nonvolatile compounds are not generally considered as inhalation hazards unless they have extreme toxicities (i.e. chemical nerve gases).

By using host-guest complexation, the P° term may be effectively lowered when the volatile component is included by the molecular trap (host). This, we believe, will allow enhanced sensitivity for detection of specific volatile components. Additionally, since the molecular traps are selective in their ability to form stable neutral guest-host complexes, there exists the distinct possibility of using them to develop selective molecular size mass detectors.

EXPERIMENTAL

In this study, the frequency response of the coated crystals was monitored under various combinations of experimental conditions in order that the host-guest interactions might be studied.

In order to attain high sensitivity, the crystal and its oscillator circuit must be very stable with low drift throughout the period of the experiment. The frequency of crystal oscillation is not usually measured directly but is mixed with a frequency reference. The experimental apparatus housed three piezoelectric crystals coated with host molecules, [6.6.6]cyclophane hexalactam trimer (Figure 1) and one crystal coated with a gas chromatographic absorbent. A reference piezoelectric crystal was used to give a beat frequency between it and the coated crystals.

According to the manufacturers specifications (4), the crystal oscillators have a frequency stability of ±0.0025% over an operating temperature range of 0 to 70°C. This allows the sensor to be operated over a wide range of temperatures to accomodate the characteristics of the analyte under investigation. The temperature of the piezoelectric crystals within the apparatus was controlled to ±0.03°C using a microprocessor-controlled Peltier device (5). The resulting analytical system has a frequency stability of ±1Hz/hour.

Nitrogen gas is introduced into the PQM apparatus and a baseline frequency is obtained. Gaseous guest molecules ($CHCl_3$, $CHCl_2$, etc.) are impinged upon the coated crystals and the frequency response is monitored (exposure time). After the appropriate exposure time, the analyte gas is turned off and the nitrogen gas is turned on for the desorption of the solute vapors.

The experimental parameters varied during the course of these experiments were: the amount of coating, the concentration of the various guest molecules, the temperature and exposure and desorb times.

RESULTS and DISCUSSION

Figure 2 shows a plot of the frequency response of a crystal sensor versus a reference crystal to a given gas analyte over time. Sorption of the analyte is observed during the exposure time. A permanent increase in the baseline frequency of a piezoelectric crystal was evidence of the formation of a host-guest complex. This change in baseline frequency did not occur for molecules which are known not to form a complex with the host. The original baseline frequency of a coated crystal was restored upon mild heating within the apparatus which indicates the inclusion process is reversible at elevated temperatures.

Figure 3 shows a typical plot of the temperature controlled by the Peltier device during the experiment. The precise control of the temperature will allow greater crystal stability and accurate frequency measurement.

It must be emphasized that the potential is great for development of truly portable vapor detectors for volatile substances that have specific responses to certain molecular structures. Preliminary data lead us to conclude that the gas phase molecular trapping reaction works. However, much additional research must be done before the analytical advantage of selective molecular traps can be realized. In addition to studying the use of neutral organic complexing agents as selective molecular traps, much instrumental development work must be done on the microbalances to achieve a truly portable analytical device.

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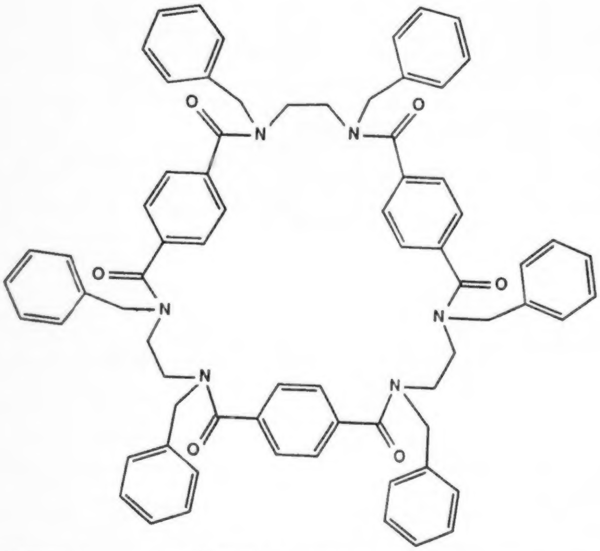

Figure 1. [6.6.6]Cyclophane Hexalactam Trimer

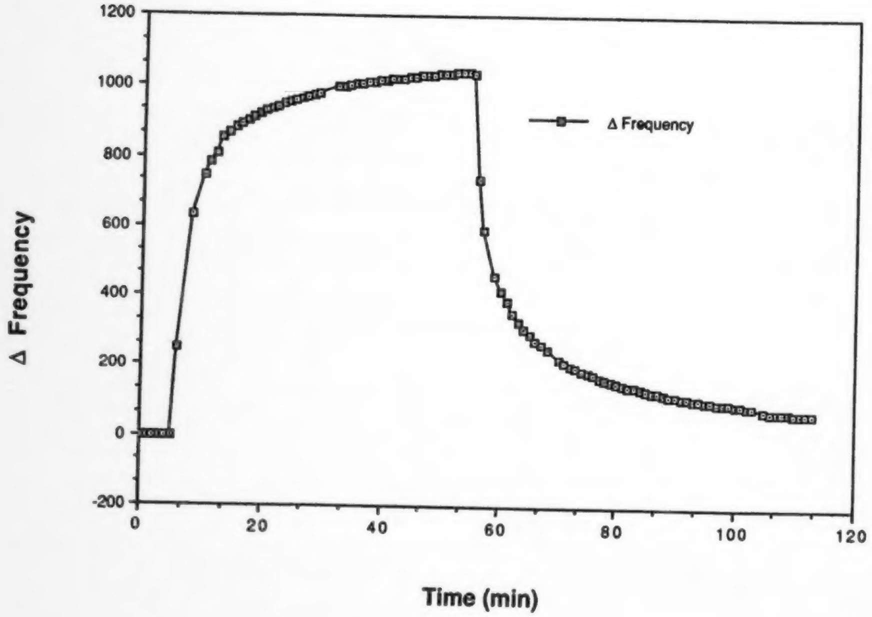

Figure 2. Frequency Response for Lactam-Coated Crystal

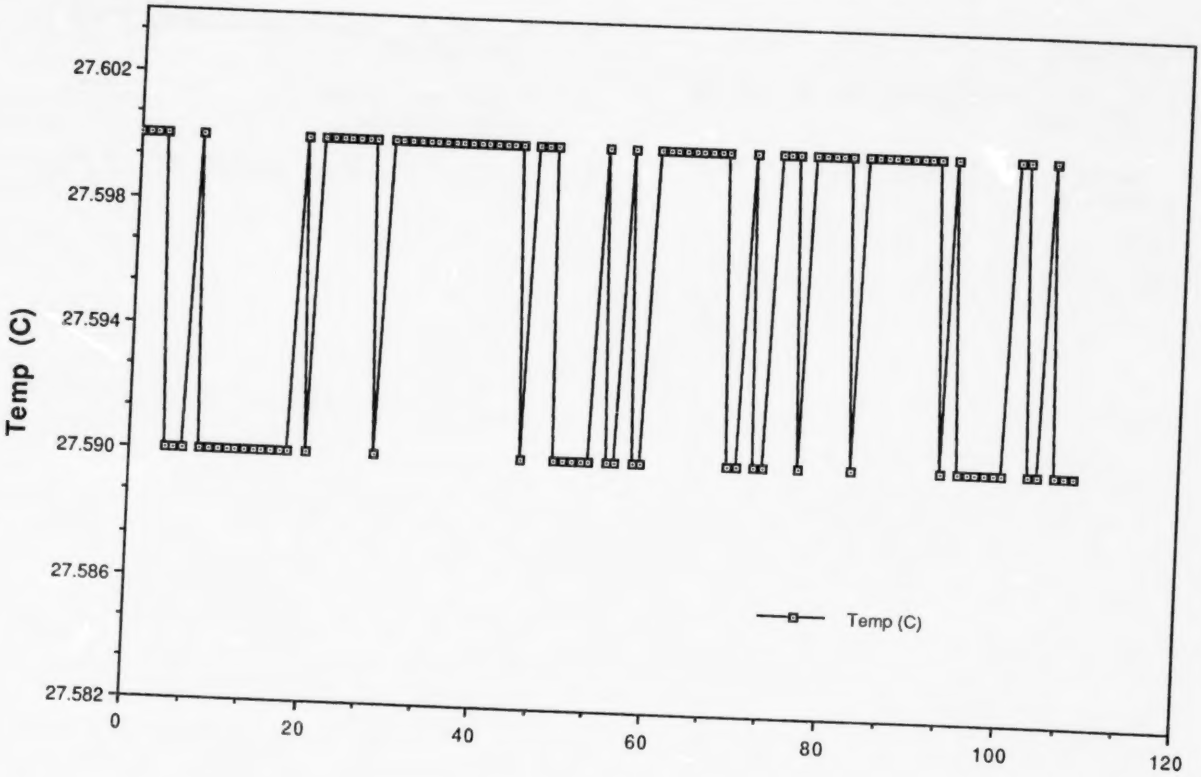

FIGURE 3. Peltier Controlled Temperature Profile

DISCUSSION

MARTIN SPARTZ: You were mentioning that you thought that the mechanism for the sample was there. But did you check the frequencies in the FTIR to see if they had been shifted, due to any binding that might give us specific binding to a certain compound?

ED OVERTON: They are shifted very slightly. That's not a perfect overlay. The molecular weight of chloroform is about 120, and the molecular weight of lactam is 1,100. You don't really have much chloroform relative to the total carbon material there. We were seeing really small changes, and I'm sure we weren't getting 100% of the molecule complex. So it was pretty hard to tell whether we were getting much of a shift or not. Basically, what we were hunting for was evidence for a gas phase reaction, and the spectra, in my opinion, indicated that yes, the bands were in about the right spot. They were changed very slightly from the Sattler spectrum.

INTRODUCTION TO THE X-RAY FLUORESCENCE SPECTROMETERS SESSION

Harold Vincent, Chairperson

X-ray fluorescence is already being used in the field. What we're here to address is to determine how much it's being used, the good things, the limits and where we need to improve. What do we need? What does the client need, what does the experimenter need, and what do the analytical samplers need?

What is the major challenge in application of XRF under field conditions? It seems to be how we can use tools on the shelf better than we're using them now. A lot of these tools have been on the shelf for 10 years without much improvement but we still aren't using them as much as we should. I think you're going to see an acceleration of their use in the near future in field screening application.

There are several questions to ask. What are the directions that we should take in putting together modules that will do the job for us? Are we really using modules off the shelf to our best advantage? Another question is, when do we go in the field? You can go in the field as a screening outfit, prior to any kind of sampling effort, and provide useful information. You can go in at the same time that samples are being collected and sent back to the laboratory. You can go in during a remedial effort. You can be part of the control system. You can go into a hazardous waste site after the sample collection effort.

The information you provide by X-ray fluorescence may be a control, a final wrap-up, or a traverse. It is usually provided in conjunction with samples that are taken to a base laboratory. Many variations are possible depending on the problem at hand.

Now what are some of the other needs? What equipment do we need to have in hand to do this? I made a list of items that I think should be fulfilled, areas that we should be looking at to help fulfill these needs.

The EPA Contract Laboratory Program (CLP) has a target list chosen to be effective in toxic waste measurement – but it doesn't include very much of the periodic table. It's a rather restricted list from an X-ray standpoint.

There are many elements that could be measured by X-ray fluorescence in the field that are not measured currently, because they either haven't been a problem, or they occur in very low amounts. Detection of low concentrations could be a problem that we'll need to look into.

Many elements that are involved in manufacturing processes – and there are a number of them not on the current CLP list – could become toxic problems in the future.

Most of the heavier or high atomic number elements, could be measured by some of the conventional methods now being used. ICP will measure most of them. Gases, like radon, aren't likely to be measured by X-ray. We could do it by X-ray if it were captured. You wouldn't be able to do that by ICP. We have a unique advantage in measuring some of these by X-ray fluorescence.

X-ray excitation is a critical issue in the field, with portable a system. Safety is a prime parameter. We can't put a person out on a hazardous waste site, or possible hazardous waste sites, without that person being protected from us, as well as from whatever environment he or she encounters.

If we use an instrumental source, we have off/on capability of removing any excitation safety problems emanating from X-rays. If we use isotopes, we've got to make sure that we can shield those isotopes. We've got to make sure that we don't leave radioactive or toxic residue of any kind behind.

The intensity of the X-ray flux is an important parameter in terms of X-ray detectability and in turn elemental detectability. The energy level is important. It is necessary to exceed a threshold energy level for excitation for each of the elements. This can be used as an advantage, and it can be a disadvantage at times; but for the target element of choice, you have to have enough energy to do this excitation, you have to have enough intensity to get a number of counts, so that you can make the measurement.

In regard to the spectral band of the excitation, the choice is between a monochromatic source or a polychromatic source. Most sources are broad-band unless some kind of filtration, or secondary tartet is involved.

When we put in secondary targets, we usually have losses of intensity. We've got to address these problems, because one of the other battles we're fighting continuously in the field is detectability. We've got to be able to detect low amounts of some of these inorganic materials.

The stability of the excitation is important. For radio isotopes, you never have problems with power fluctuations. You may have problems with the short-lived isotopes that must be corrected for output on the short term. If you use an instrumental X-ray, a tube source, then you have power requirements and you may have stability concerns. If the X-ray source is an isotope, you can be energy selective, and there is a lot of advantage there.

The special characteristics for sources would include the size and shape, and anything that allows you to get on site with a small package, do the job, and get off with a small package intact.

Any time you put a large package on a hazardous waste site, you may have to throw it away. If you contaminate the instrument on site, you may actually lose it. Don't put $50,000 into a machine you might leave behind.

The efficiency of a detector is involved with detectability. The measurements for many elements may be at a minimum level of detectability, where there is uncertainty. We need to be able to measure small amounts of toxic materials. That could be very, very important.

The geometry of the detector is related to detectability as are resolution and discrimination. Can I tell lead lines from arsenic lines? The energy range may limit detector application? If you have a detector that has a range cut off, it will allow some discrimination.

Durability of a detector is very important at a hazardous waste site. We may have one of these in the field. You can't easily replace it on site. If it's a crystal, if it cracks, it may yield improper information. If it's a gas, and if you knock it against something and it leaks, it's gone. If there is a hot wire in there and it breaks, it's gone. You may have to leave it behind. You may not be able to afford two of them on site at the same time. So cost is a very important thing.

If you have an instrumental source, high voltage is a requirement, and you always have requirements for power to get signal transmission.

Does the system answer the question that was being asked in measuring on site? Suppose you have a material that's water soluble and moving through the ground, and you come in and measure the total amount of that material. How do you discriminate between mobile amounts and the total? How sound is the sampling schemes to answer the questions? Particle size is very important. It has much the same effect as coatings do on X-ray emission.

How do we get a sample that represents a heterogeneous material? The more heterogeneous or coarser it is, the larger sample we need, or the more samples we have to take to represent a larger sample.

If we put an XRF machine on a robot, send it onto a hazardous waste site, and the sample has to be mixed up in some fashion, how do we do that?

How do we present it (presentation to the excitation). Is it flat, is it curved, does it have to be very smooth? A lot of this will depend on the penetration of the X-rays and the energies of the exiting X-rays. Presentation excitation is part of the sampling considerations for the site.

We need some knowledge about the sample make-up, which would let us know something about matrix effects ahead of time. If we know that ahead of time, we can be much more effective in designing standards and references, as well as our whole plan of X-ray analysis.

How do we mark the location when we aren't taking a handful of dirt out of the soil for every sample that we're measuring. We're leaving it there, and measuring it *in situ*.

Data have to be collected and presented, either to somebody for data handling or to a client for whatever use he wants. How do we do that? The advantages that we have in the last ten years in this field are advances in the data handling area. The computers have gotten smaller, the memory is cheaper, and the trend is continuing to move in those directions. I think we'll see more advantages and more advances.

We need to make data management as automatic as possible. A person is responsible for collecting data, for making sure that it gets the right tag, that it gets transmitted, or recorded, and that he can verify that data are good.

How do you get hard copy out of a little black box that you carry out in the field? You may not want to take your gloves off to write with pencil and paper. Maybe you can punch buttons here. How clever are we going to be in getting that hard copy?

How do we know when to reject data in the field and reject bad data. This is like crossing off a page in your laboratory notebook. How do we know when to cross off that page? One advantage is that taking these measurements is rapid enough to allow for repetitive tests.

And a word about quality assurance. It includes a lot of buzz words – including initial and continuing calibration. These are common buzz words with the CLP program. They are no less important with field screening.

Suppose you are in the field, and somebody has just dug an acre of dirt down to about five feet deep, and carted it off in trucks. Somebody comes back and says that you carted off a lot of pretty good top soil. You say it was hazardous, and he says, can you prove it to me? How do you know? How well do you know that? You've got to have some pretty good quality assurance information to prove you acted correctly.

We've got to have proper calibration, we've got to have it referenced to standard materials if possible. We've got to keep good records. We've got to verify that the samples were where they were.

We've got to be very sure of what we put down on paper, that it's accurate, that it solves the problem, and that we can back it up.

These are just some of the parameters we can ask our speakers about in this session.

APPLICATION OF FIELD-PORTABLE XRF TO HAZARDOUS WASTE CHARACTERIZATION

Richard K. Glanzman

CH2M HILL
6060 South Willow Drive
Greenwood Village, Colorado 80111-5112

ABSTRACT

Refinement and miniaturization in instrumentation have allowed the development of field-portable, x-ray fluorescence (XRF) instrumentation. This XRF capability fills an important gap during field sampling--the collection of representative samples to define the extent of inorganic contamination. Using a portable XRF, analyses can be performed in the field, allowing for immediate screening of many samples. Two instruments have been field tested. Both have advantages and disadvantages. Ideally, both are capable of detection limits in the tens-of-parts-per-million range for most metals, depending on the media and its physiochemical characteristics. In the field, both instruments have been shown to be capable of nondestructively and quantitatively determining concentrations of most metals in soils, sediments, and rocks below the commonly applied action levels for cleanups.

INTRODUCTION

Use of field-portable x-ray fluorescence (XRF) instrumentation to determine the extent of metal contamination reduces the cost while increasing the probability of obtaining representative samples from hazardous waste sites. Refinement and miniaturation in electronics have led to the development of several instruments that weigh less than 25 pounds, can be placed into a backpack, and taken to the sample site. These instruments allow field personnel to qualitatively to quantitatively determine the concentration of a suite of metals in many different types of media at the site and to differentiate between background and contaminated media. Media may include soils, stream sediments, tailing, slags, water, vegetation, paint, landfill material, structural steel, cement, etc. This allows the field personnel to obtain statistically representative samples to define the nature and extent of metal contamination.

Sampling design takes place in the field, based on observed concentration rather than on an assumed contaminant source and dispersive characteristics. The spatial distribution of target metals is defined in the field, allowing a more accurate selection of media and metals to be analyzed.

Measurement times are relatively fast (usually one to two minutes), and analyses do not alter the media being measured (nondestructive). Therefore, integration of XRF instrumentation into a field effort can reduce the number of samples to as little as 10 percent of those required by conventional field-sampling techniques in the first (and sometimes only) sampling effort.

Field-portable XRF instruments have been utilized in the minerals industry for approximately 10 years. One such instrument was developed and used on the Mars Lander. Instrument size and detection limits have decreased as the instruments became more sophisticated and simpler to operate. XRF instruments can be utilized in both Level II and Level III analytical work as defined by Furst et al. (1), depending on calibration and sample preparation. Preliminary evaluation or screening (Level III) involves minimal calibration and sample preparation. Remedial Investigation (RI) and Feasibility Studies (FS) (Level II) require calibration and may require some sample preparation. The precision, accuracy, and detection limits required for litigation and enforcement support (Level I) exceed the analytical capability of the field-portable XRF instruments. The most cost-effective use of these instruments is at Levels II and III to screen samples for laboratory analysis. However, the instruments can be effectively employed in defining metals concentrations for Emergency Response and removal actions as well.

Documented use of field-portable XRF instruments began in 1985(2)(3). The Smuggler Mountain Site near Aspen, Colorado, was the site of the first published use of one of these instruments to determine the boundaries of criteria levels of 1,000 milligrams per kilogram (mg/kg) lead and 10 mg/kg cadmium in soils and tailing (3). The same site was used to evaluate a prototype field-portable XRF instrument (4). A new calibration technique (5) and published use on nonmining-related media (lubrication oils) (6) were reported in 1988. The use and range of application have expanded to use in determining the presence and amount of lead-based paint in homes and the areas of phytotoxic soils. CH2M HILL is currently using the instrument at four sites in the western U.S. in Level II and III capacities.

PRINCIPLE OF THE XRF INSTRUMENT

Field-portable instruments are produced currently by at least five companies. The same basic principles are used in these designs (Figure 1). The instruments utilize the energy dispersive x-ray (EDX) technique developed in the 1970s to produce a light-weight field instrument. The technique involves the use of low-level radioactive isotopes to excite the elements in samples. The four commonly used isotopes are iron-55, cadmium-109, curium-244, and americium-241. Selection of the isotopes depends on the metals (elements) of interest. For example, iron-55 is best suited in determining the lighter elements (silicon through vanadium) in the periodic table. Source activity usually ranges from one to 100 millicuries.

The source excites the atoms of elements in the samples, which give off an element-specific wavelength of energy (fluoresces) that impinges on the gas proportional tube (GPT). The GPT converts energy into a signal that is amplified and processed through a microprocessor. The sample emits the spectra that are recorded as counts at energy levels specific for the elements making up the sample. The number of counts at a specific energy level is proportional to the amount of that element exposed to the radiation source. The technique dates from the early 1900s, but the development of a field-portable instrument required current technology.

The number of counts in a specific energy level requires correction for background, interference, etc. and is reported as an index number (or intensity). The index number is then compared with calibration standards for each element of interest to develop a calibration curve relating index numbers to concentrations for each element.

VARIABLES IN THE ANALYSIS

The goodness of fit (linear regression line) of the index number/concentration relationship for each element is a function of radioactive source strength, particle size, sample matrix, sample surface characteristics, and other elements and their abundance in the sample. The calibration standard should match these sample characteristics as closely as possible to produce a high level of precision and accuracy. The more uniform and homogeneous these characteristics are in both the standards and the samples, the better the calibration and the results will be.

Source strength is a function of both initial manufactured activity and the isotope's half life. Year-to-year measurements of a specific element in a specific sample would not change appreciably (other factors being held constant) if the source were an americium-241 isotope with a half life of 433 years. However, a cadmium-109 isotope source with a half life of 1.3 years has only half its initial source energy after 1.3 years. Cadmium isotope sources usually need replacement at least every other year, but use also depends on initial source level and concentration of specific elements requiring analysis.

The sample particle size should be as homogeneous as possible, with smaller particle sizes giving better correlation between index numbers and concentrations. The 200- to 300-mesh (clay size) particles give the best analytical results, with correlation decreasing as particle size and variability of particle sizes increase. Qualitative-to-semiquantitative correlations can be achieved with 80-mesh (sand size) particles if the element is a major element and/or is dispersed homogeneously throughout the sample.

The matrix of the sample can be expressed as the average atomic number and range of atomic numbers making up the sample. Matrix is the dominant factor determining the depth of penetration and the response from the sample. Depth of penetration can range from several centimeters to just a few microns, depending on the matrix (Figure 2). Water and hydrocarbons have the highest depths of penetration and some of the best calibration curves because of their low average atomic number when a very narrow range of atomic numbered elements makes up the major proportion of the sample. In dense minerals, such as pyrite (iron sulfide) and galena (lead sulfide), the depth of penetration is in the tens-of-microns range because of the minerals' high average atomic numbers, but the precision and accuracy may still be excellent if all the other factors are held constant. Surficial chemistry is particularly important on these heavier minerals. The field XRF analyses can be looked upon as complementing laboratory work because the surficial layers analyzed by the field instrument are most likely to be the short-term dissolved portion from any solid matrix.

Field media can be visualized in a fashion comparable to an average atomic number. Plants, containing mostly water and carbon compounds, with low atomic numbers have the highest proportional depth of penetration. The penetration decreases with denser materials. The lack of sample preparation necessary to analyze plants and fine-grained soils means that the XRF analysis may be a more accurate analyzing technique. Sample preparation is commonly difficult and can drive off parts of element concentration from plants. Dissolution techniques for preparing soils, rocks, and other solids for analyses may not put all of particular elements in solution. XRF is a total element analysis procedure that does not physically alter the sample and does not depend on the compound chemistry containing the element.

The smoother or more regular the sample surface, the better the correlation between index numbers and concentration. A painted surface is almost ideal. Water and soils are commonly placed in a cup with a thin polypropylene or mylar window stretched across the base of the water or soil column. This window, too, gives very high correlations. Rocks with very irregular surfaces will give poor correlations.

Elements associated in a sample by overlap can cause either enhancement, adsorption, or interference. Adjacent elements in nearly equal, low concentrations can be difficult to analyze because of overlap between their peaks. For example, nearly equal, low concentrations of copper and zinc would be difficult to separate and would cause a high detection limit. Similarly, nearly equal, low concentrations of arsenic and lead are difficult to determine because the major peaks for both elements have approximately the same energy level; their concentrations must be determined by using the much smaller, secondary peaks.

EXAMPLE CALIBRATION CURVES

Figures 3, 4, and 5 show calibration curves for iron, lead, and cadmium, respectively, that were developed using field-portable XRF instruments. Iron is commonly present in percent-level concentrations, particularly in mining districts. The iron calibration curve (Figure 3) represents iron in soils and stream sediments in one such district. Another curve was developed for pyrite-rich tailing that resulted from milling to recover galena. The lead calibration curve (Figure 4) and the cadmium calibration curve (Figure 5) also represent soils and stream sediments. In addition, the cadmium calibration curve indicates the low detection limits (on the order of tens of mg/kg) that can be achieved using the field instruments without sample preparation.

APPLICATIONS AND RESULTS

The potential application of the field-portable XRF instruments can be almost universal in that virtually any media that contains elements heavier in atomic weight than silicon can be qualitatively to quantitatively analyzed. In a qualitative sense alone, the instruments have been proven to be able to:

- Determine background areas from contaminated areas
- Differentiate uncontaminated soils from soils containing phytotoxic concentration of metals (and to identify the metals)
- Distinguish homes painted with lead-based paints
- Distinguish and rank water samples containing as little as 5 milligrams per liter zinc and copper
- Determine volume of contaminated material for removal

Figure 6 illustrates one example of using the field-portable instrument in a qualitative sense. Sampling drill cuttings for metals contamination is commonly done by visual judgement or by compositing equal lengths of core or cuttings. In this case, cuttings from a 40-foot monitoring well installation were qualitatively analyzed (scanned) using the XRF instrument. Although the iron indicates two well-defined peaks that were quite evident visually, lead, zinc, and copper did not mimic the iron concentration. Only the upper 5-foot sample contained appreciably higher metal concentrations. Copper and zinc were similar in their distribution. Lead, although similar in the upper part of the section, increased at the base, where iron is lowest.

This information can be generated in about 15 minutes, allowing the sampler to focus on sampling the elements and element concentrations where they provide the most information. The samplers know the metal distribution and relative analytical results when they leave the field. Interpretations are made immediately in the field instead of trying to make them from laboratory results, weeks to months later, using field notes and memories as a guide.

Qualitative results are developed quickly and easily, but can be developed into semiquantitative-to-quantitative results, increasing the analytical description of the field setting with fewer laboratory samples. Samples are qualitatively analyzed in the field to document the representative sample sets, using statistical distribution calculations. These calculations can be as simple as definition of the "normal" distribution of metal concentration or as complex as geostatistical kriging--all performed using index numbers. When a representative suite of samples has been analyzed, calibration curves can be developed and the index number data can be assessed. Semiquantitative analytical results are common. Quantitative results can be achieved using relatively homogeneous media.

Figure 7 presents an example of using the field-portable XRF instrument for quantitative determination of metals concentrations in mine wastes occurring in residential areas. The lead data were developed from mine wastes in a large mine-waste pile adjacent to four homes. The data indicate a very wide range in lead concentration in the fine-grained mine waste (1,210 to 210,000 mg/kg). No galena was visible, even using hand lens, so the percent-level concentrations may be secondary lead sulfates, carbonates, and/or oxides. Lead calibration curves, similar to those in Figure 4, were developed from the laboratory data that resulted from samples collected from this and other mine-waste piles. Similar plots were developed for copper, zinc, and other metals.

Figure 8 illustrates a second example of the quantitative determination of metal concentration: analyses performed on a large slag pile. Slag is a dark-colored, dense, glassy residue of the smelting process. Smelters in large mining districts that continue to operate for a long time change with improvements in technology, commodity prices, and ores processed by the smelter. These changes are reflected in the metals remaining in the slag, which are slowly leached from the slags by the weathering process. The problem is similar to that of the mine waste--collecting a documented, representative sample from these homogeneous-appearing piles. Collecting slag samples is difficult because they have to be chiseled from the large glass mass. The XRF indicated that the metals concentrations in this particular pile were relatively homogeneous; however, the range of lead concentrations almost covered an order of magnitude (13,600 to 95,000 mg/kg). Also, the north and east sides of the slag pile had lead concentrations below 20,000 mg/kg, while most of the mass contained between 20,000 and 30,000 mg/kg lead. A grab sample from the western edge of the slag pile would have exaggerated the lead concentration by a factor of 4 to 5 (25,000 versus 95,000 mg/kg). On the other hand, grab samples collected on the eastern or northern edges would have underestimated the lead concentration by a factor of about 2. The index numbers allowed the samplers to collect fewer, but more representative samples, and to obtain a better distribution of sample data for interpretation. Other metals concentrations were simultaneously determined with lead and plotted in the same manner.

CONCLUSIONS

The field-portable XRF is an under-utilized analytical screening tool that allows determination of the nature and extent of contamination in the field, collection of representative samples, and documentation that representative samples were collected. The instrument simultaneously and nondestructively gives a total element qualitative-to-quantitative concentration of a suite of elements in the field in a matter of a few minutes. The instruments have been used at inorganic contamination sites involving metals, but applicability can extend into halogenated organic sites as well.

ACKNOWLEDGEMENT

The author wishes to acknowledge the contributions received from Alan Seelos with Aurora Tech Instruments and John R. Rhodes with Columbia Scientific Industries Corporation.

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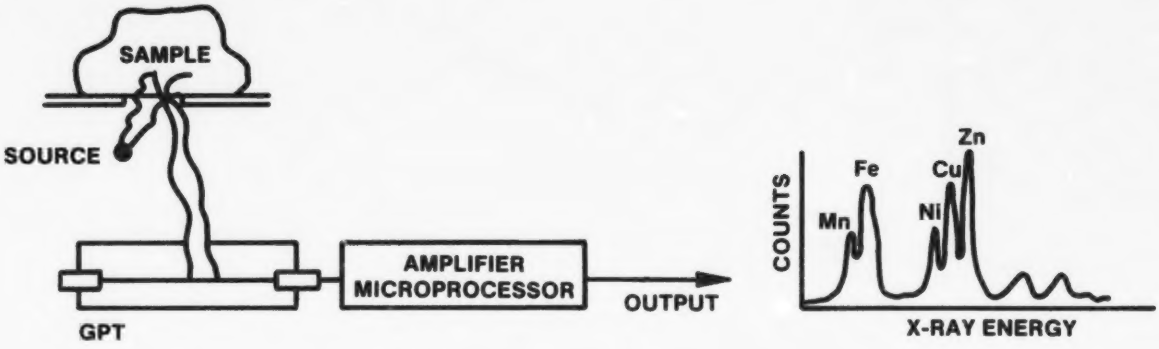
SAMPLE
SOURCE
GPT
AMPLIFIER
MICROPROCESSOR
OUTPUT
COUNTS
Mn
Fe
Ni
Cu
Zn
X-RAY ENERGY

FIGURE 1. SCHEMATIC INDICATING THE FIELD-PORTABLE XRF ANALYTICAL PROCESS.

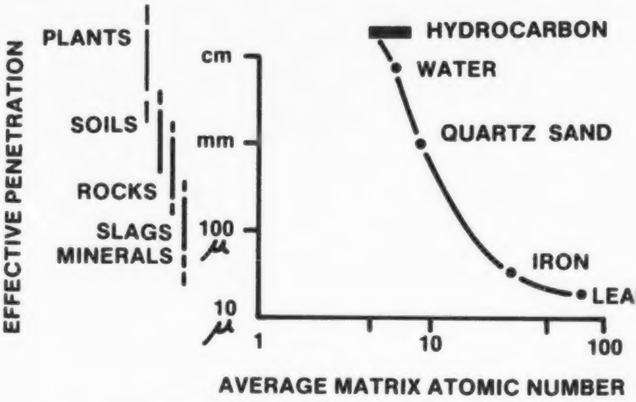

FIGURE 2. APPROXIMATE RANGE OF EFFECTIVE PENETRATION AND RESPONSE FROM SAMPLE MEDIA.

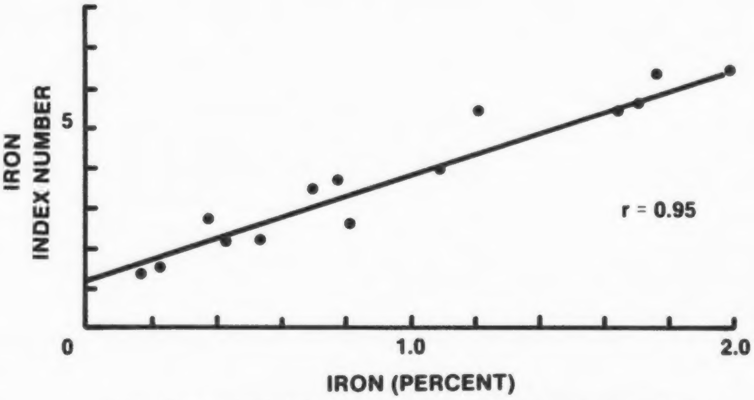

FIGURE 3. IRON CALIBRATION CURVE BETWEEN INDEX NUMBER FROM A FIELD-PORTABLE XRF INSTRUMENT AND LABORATORY RESULTS ON THE SAME SAMPLE.

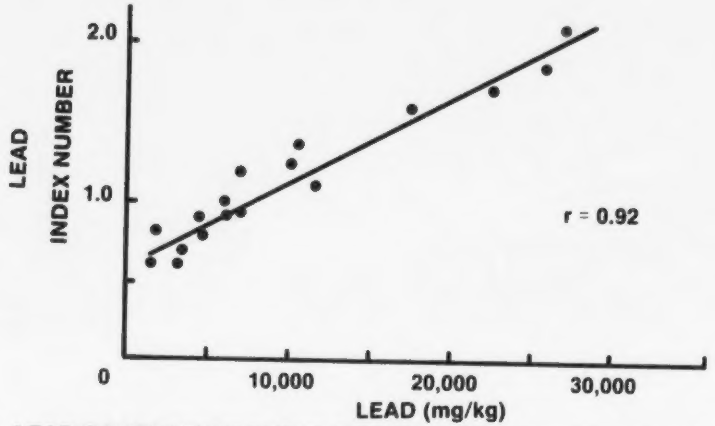

FIGURE 4. LEAD CALIBRATION CURVE BETWEEN INDEX NUMBER FROM A FIELD-PORTABLE XRF INSTRUMENT AND LABORATORY RESULTS ON THE SAME SAMPLE.

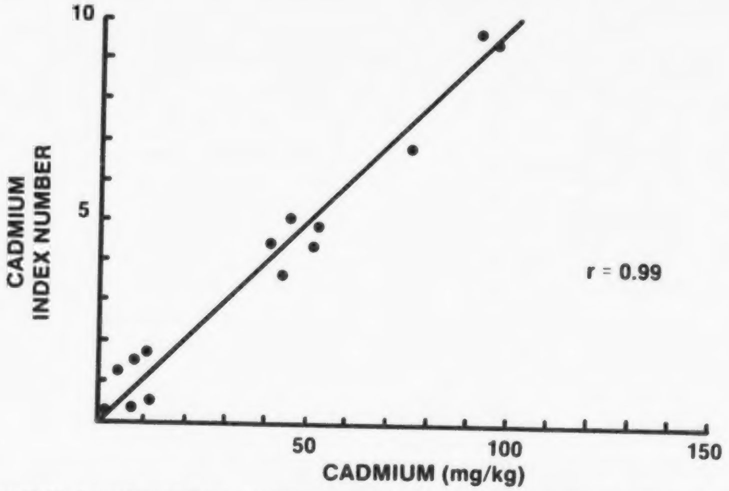

FIGURE 5. CADMIUM CALIBRATION CURVE BETWEEN INDEX NUMBER FROM A FIELD-PORTABLE XRF INSTRUMENT AND LABORATORY RESULTS ON THE SAME SAMPLE.

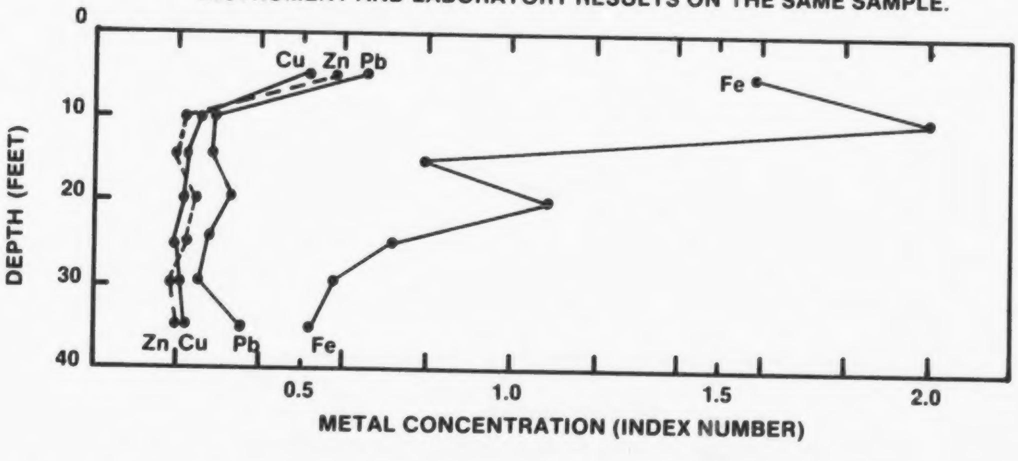

FIGURE 6. COMPARISON BETWEEN IRON AND THE METALS COPPER-LEAD-ZINC IN DRILL CUTTINGS USING A FIELD PORTABLE XRF.

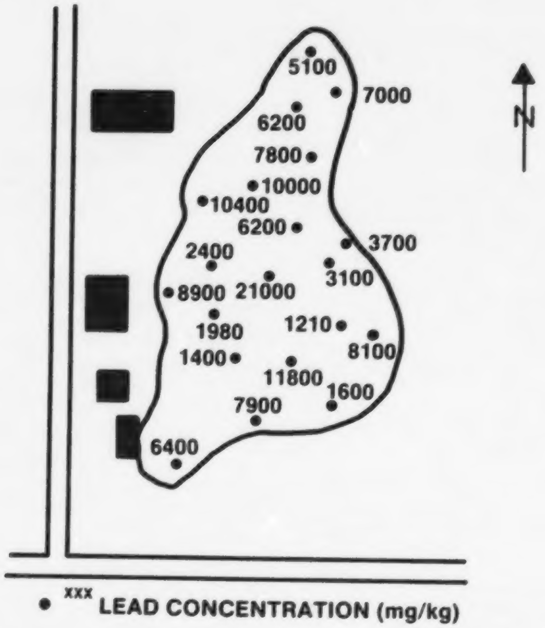
5100
7000
6200
7800
10000
10400
6200
3700
2400
3100
8900
21000
1210
1980
8100
1400
11800
1600
7900
6400
N
• xxx LEAD CONCENTRATION (mg/kg)

FIGURE 7. LEAD CONCENTRATION IN A MINE WASTE PILE DEVELOPED FROM A COMBINATION OF XRF AND LABORATORY DATA.

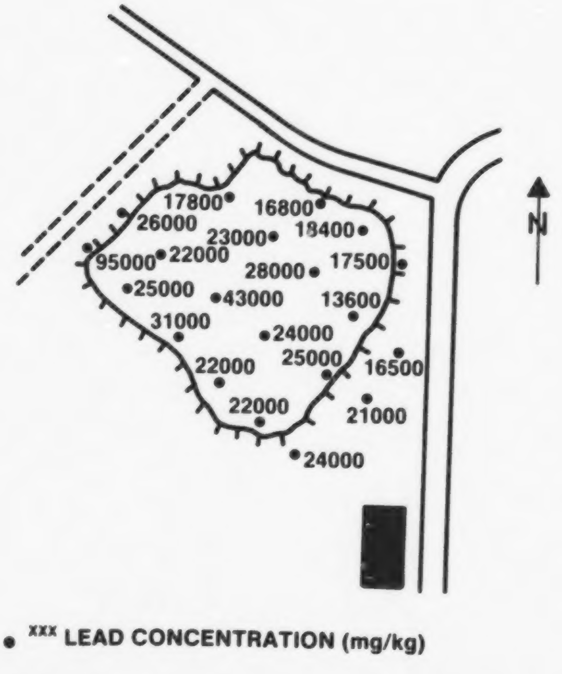
17800
16800
26000
23000
18400
95000
22000
28000
17500
25000
43000
13600
31000
24000
22000
25000
16500
22000
21000
24000
N
• xxx LEAD CONCENTRATION (mg/kg)

FIGURE 8. LEAD CONCENTRATION IN A SLAG PILE DEVELOPED FROM A COMBINATION OF XRF AND LABORATORY DATA.

DISCUSSION

ALAN CROCKETT: What kind of sample preparation was used.

RICHARD GLANZMAN: The only sample preparation used on the mine waste, was taking the big "goopers" out by screening down to an 80 mesh.

We found that if we can get an 80 mesh, for screening purposes, that's perfectly adequate. The rest of the data were developed on soils and stream sediments that were 80 mesh-type stuff, or less. There isn't much improvement below 80 mesh.

HAROLD VINCENT: You have three geologists sampling there. Did they actually take those samples, were they grab samples, or pulverized samples?

RICHARD GLANZMAN: They represented both soil and rock samples, because we were interested in some information on what was being wasted off the outcrop, as well.

HAROLD VINCENT: On the lead mine waste, did you do any kind of distinction or discrimination against soluble vs. insoluble lead.

RICHARD GLANZMAN: That's a good question. The XRF is a totalizing instrument, so that the sample fluoresces from the element itself, and the form of the element that is present within the substrate that you're using is not terribly important, except from a matrix standpoint.

We use X-ray diffraction to determine the mineralogy, and on many of these, we have done that, XRF being the totalizing type of instrument, it didn't discriminate between the two, other than the calibration curves, when we wanted to clean those up.

HAROLD VINCENT: You didn't run any solubility tests separately?

RICHARD GLANZMAN: Yes, we did that to see whether there was some soluble lead. Although we generally consider lead to be fairly insoluble, we had some samples from one waste pile that on bottle-roll leach tests with distilled water were showing 44 ppb.

So it can be very soluble, and that's the reason we also did some X-ray diffraction. We found that a complete suite of lead oxidation products were there. We had galena, oxides, carbonates, and sulfates. They were all present, and we did not think that it was going to be that high when we initially did the test.

HAROLD VINCENT: Could you say something about the calibration and the standards you used to back up your information?

RICHARD GLANZMAN: When we're out on the site, we do a lot of scanning. When we use the instrument in a scan mode, we use it for, say 10-, 20-, 30-second counts, just to get an idea of the limits and what the dispersion pattern looks like. Then we will go to the one-minute counts, to get serious about what we're doing and what samples we're picking up.

We will collect the sample and use the XRF on the sample that we send to the lab. When we get our laboratory results back, we do an index comparison with a least-squares fit against their concentrations. In this manner, we do use standards out in the field.

In the morning we run a suite of samples to make sure the instrument is functioning. In the evening, we run that same suite of samples. The suite of samples has been analyzed so that we know the statistics and the variability of the concentration that we're after. So in that way, we're running an instrument that we know is functioning. But we don't know that the matrix is exactly the same. The instrumentation has some limitations, as little as I would like to acknowledge that.

THE USE OF TRANSPORTABLE X-RAY FLUORESCENCE SPECTROMETER FOR ON-SITE ANALYSIS OF MERCURY IN SOILS

David J. Grupp, David A. Everitt, Raymond J. Bath, Ph.D.
NUS Corporation
Richard Spear, Ph.D.
U.S. Environmental Protection Agency, Region 2

X-ray fluorescence is gaining increased acceptance as an analytical technique for the determination of inorganic compounds in environmental samples. X-ray fluorescence provides a fairly rapid nondestructive analysis with minimum sample preparation, allowing results to be rapidly generated and used on-site to make project related decisions. A transportable x-ray fluorescence spectrometer was used to analyze over 500 soil samples for mercury to determine the lateral and vertical extent of mercury contamination at a hazardous waste site.

Preparation and analysis of each sample was performed on-site and the results generated were immediately used by the site project manager to make critical decisions on the number of samples to be collected, the depth of subsurface contamination and the lateral extent of contamination. A percentage of the samples collected and analyzed were also analyzed by a fixed base laboratory to verify the results generated by the XRF technique.

The paper presents mercury results generated using the transportable x-ray fluorescence spectrometer, and presents a comparison of the XRF results and the fixed base laboratory results. The decision making process utilized at the site is also presented along with an examination of how the transportable XRF spectrometer was used to make critical on-site sampling decisions.

DISCUSSION

AVRAHAM TEITZ: What standards did you send? Were those the ones that you mixed yourself, or were those the ones that you had gotten from outside, that you had sent to the various laboratories?

RAYMOND BATH: The only standards we sent to the laboratory were those made up ourselves. We did not send any standards to the lab, because at that time (a little over a year ago) there was only one standard available from the Environmental Systems Laboratory here in Las Vegas. In the low ppm range, the standards are just not available.

DOLPH CARDENAS: When you were drying your sample, didn't you drive your mercury off by volatilizing it?

RAYMOND BATH: That was a real concern, but it does not since we air dry it. This was the first way proposed by Kevex, if you read their manuals. We produced our own manuals for Region II.

Kevex used an oven at 70°, so we compared it with an oven at 70°, with letting it stand overnight and drying, and with a microwave pulse. You can pulse dry it. You don't do it all at one time at full power but use a 50% or 80% power level. We have not found any mercury loss.

DOLPH CARDENAS: I'm assuming, then, that the CLP Laboratory used standard CLP techniques.

RAYMOND BATH: They used atomic absorption and analyzed the sample. It was a specialized test just for mercury so I don't believe they used a standard digestion procedure.

DOLPH CARDENAS: I believe it's just a leaching technique, and it's for a total mercury. Perhaps if they had used a total digestion, they would have gotten closer to your numbers. We have seen roughly a two-to-one relationship, as you demonstrated.

RAYMOND BATH: There is a real problem with this. The site has been investigated for a long time, and one of the questions that was originally brought to me was how to distinguish organic mercury from inorganic mercury.

So we tried about two and a half years ago at this site, before we had the XRF, taking soil samples and trying to get organic analyses done – a total digestion and a leaching digestion, and looking at the difference between the two, to see if it was organic mercury.

The results were very unsatisfactory. We couldn't tell anything. I have not tested the microwave digestion, and I don't know what that would do with the mercury.

BOB NOLKOFF: What kind of data reduction program did you use on the Kevex? Was it fundamental parameters, or did you use a least-squares fit?

RAYMOND BATH: It's a least-squares fit. Again, it's a Gaussian technique. They have a full computer, we didn't have the time to go into the computer program for it. There are a lot of variables that we played with for quite some time to get our software program to work the way we wanted it to.

One of the problems was that Kevex updated their software level halfway through the program, which was a major blow. So we elected to stay with the old software, until the project was finished.

BOB NOLKOFF: Do you know if this is all in automatic files, or was it done by hand?

RAYMOND BATH: the process is that it collects data. It's a 500-second run. At 250 seconds, it has taken the spectra, and stored it. It's processed later on.

TONY HARDING: Were you linearly correlating mercury intensity to concentration i.e., measured mercury intensity to concentration on the calibration curve?

RAYMOND BATH: No, you figure out with the secondary target using sort of a ratio effect. Because the secondary target has a constant intensity, it's sort of an internal standard.

TONY HARDING: That's only true if you ratio your mercury intensity to the intensity of the back-scattered zirconium. Is that what you did?

RAYMOND BATH: We tried each one of those techniques to get down to this level. We felt comfortable with this.

TONY HARDING: In that way, by ratioing the mercury intensity to the zirconium measured intensity, would you be able to account for things like packing density?

RAYMOND BATH: We didn't see problems with the packing density in these samples, considering the way we prepared them. We thought we might, and a considerable amount of effort went into soil preparation, to differentiate one soil type from another soil type. In packing density, we did not see that effect.

TONY HARDING: Some of the data show that your standards correlate very well between, specifically, the ESD data and the XRF data, whereas some of the actual solids don't correlate as well. Do you think that could be a matrix effect?

RAYMOND BATH: No, I think that relates to how we prepare samples for the ESD laboratory. It's a little bit different. They get a small portion right out of the homogenized jar. In the other one, we had to physically prepare that. So that sample was a little better distributed.

TOM SPITTLER: Just a couple of comments on the standardization. You were probably using the zirconium Compton and scatter peak for your normalization, were you not?

RAYMOND BATH: Yes.

TOM SPITTLER: You don't have to worry then about a packing effect. The only significant problem you might have seen in sending samples to other labs is that in any soil sample, particle size has an effect in terms of the concentration of the element being maybe more predominant in the very fine particles, as opposed to the coarse particles.

That's particularly true when you're looking at lead in soils. We have seen that in thousands of soil analyses.

So if you send off a sample that was homogenized well, but gets shaken down by the time it gets to the laboratory, and they scoop off the top part of the sample, you can have a higher concentration in the lower portion of the sample, which is the fine material.

The problem with having a laboratory properly homogenize a sample before they take their test sample out and analyze it is something we always cope with.

The data look very reasonable, on the whole, for field analysis versus lab analysis, and the more care taken with the sample preparation, the better those numbers are going to line up.

RAYMOND BATH: People underestimate the importance of sample preparation. When you're trying to do comparisons from one to the other, it's worse than apples and oranges. It's more like apples and elephants.

THE DETERMINATION OF MINIMUM DETECTION LIMITS FOR INORGANIC CONSTITUENTS IN SOIL USING TRANSPORTABLE SECONDARY TARGET X-RAY FLUORESCENCE 1. ARSENIC IN THE PRESENCE OF LEAD

David A. Everitt, David Grupp, Raymond J. Bath, Ph.D.
NUS Corporation
Richard Spear, Ph.D.
U.S. Environmental Protection Agency, Region II.

Secondary target energy dispersive x-ray fluorescence (EDXRF) is a rapid nondestructive analytical tool that has great potential for on-site screening of inorganic soil constituents at hazardous waste sites. In soil, lead and arsenic are naturally found in varying concentrations ranging from low ppm to 900 ppm for lead and 200 ppm for arsenic. When analysis is performed for arsenic contamination above background levels, the minimum detection levels (MDLs) for arsenic vary proportionally to the lead concentration in the soil. This change in MDLs is caused by spectral interference and specific absorption-enhancement effects between lead and arsenic. The use of MDLs and a review of spectra are used to evaluate the extent of the arsenic-lead interactions in a soil matrix. This presentation will identify the actual limitations of EDXRF for the determination of arsenic contamination at hazardous waste sites and demonstrate solutions to the arsenic-lead spectral and matrix interactions.

Spectral interference between arsenic and lead is described as the superimposition of first order lines of a different series. This problem can be overcome by using an alternate emission line or various computer-generated deconvolution, and pure element stripping methods to separate the regions of overlap and extract intensities. These methods are used after the spectrum has been acquired.

Specific absorption-enhancement occurs during spectral acquisition of the sample. The lead L-alpha emission energy interacts with the arsenic spectral lines causing loss in peak intensities for arsenic. This false-negative effect is concentration-dependent. As the lead concentration increases the intensity of the arsenic decreases. This phenomenon occurs when spectral lines of a matrix element and the absorption edge of the analyte are in close proximity.

Graphs are presented showing MDLs for arsenic versus lead concentrations and a comparison of peak separation techniques. Spectra showing matrix enhancement and regions of overlap will be used to identify the problems. A series of calibration matrix-correction curves are also presented. The data will be used to demonstrate arsenic-lead interactions and determine the limitations of EDXRF to arsenic screening of soils.

DISCUSSION

BOB MOLKOPF: Just a quick clarification. It can't be that lead M lines are around 2.4 or 2.5 keV. It would have to be a lead L, or some other line. It can't be an M.

RAYMOND BATH: It's a minor L.

HAROLD VINCENT: Did you do this all with a zirconium secondary target, or did you try it with other targets?

RAYMOND BATH: We have not tried any other targets at this time.

HAROLD VINCENT: Do you feel that there would be enhancement with any other targets?

RAYMOND BATH: I don't think you could get the low ppm range.

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THE APPLICATION OF X-RAY FLUORESCENCE TECHNOLOGY IN THE CREATION OF SITE COMPARISON SAMPLES AND IN THE DESIGN OF HAZARDOUS WASTE TREATABILITY STUDIES

John J. Barich, III
Environmental Engineer
USEPA, Seattle, Washington

Roy R. Jones
Quality Assurance Management Office
USEPA, Seattle, Washington

Gregory A. Raab
Lockheed Engineering Management Services Company
Las Vegas, Nevada

James R. Pasmore
Columbia Scientific Industries Corporation
Austin, Texas

ABSTRACT

Site Comparison Samples (SCS) and treatability studies are contemporary tools used in the investigation and remediation of hazardous waste sites. Each depends on the development of large volume samples which are characteristic of the most difficult conditions at a site to treat. The use of X-ray fluorescence spectrometers (XRF) to identify sample locations at a major Superfund site is described. The subsequent processing of samples into SCS materials and treatment samples is presented.

INTRODUCTION

As byproducts of a growing technological society continue to find their way into the environment, the Environmental Protection Agency (EPA) must face an ever-expanding problem of how to handle and measure the harmful byproducts. Before contaminants can be removed or neutralized, they must be characterized for type and quantity. Field-Portable X-ray Fluorescence (FPXRF) instrumentation has been shown to be useful as a screening tool for heavy metals in soils at hazardous waste sites (1,2). Instruments are smaller than their laboratory counterparts, transportable by a single individual, hermetically sealed, and provide immediate data from analyses completed with little or no sample preparation. Analyses are either conducted in a field laboratory or in situ.

The Bunker Hill Superfund Site is located in the Coeur d'Alene mining district of northern Idaho. The site is 7 miles by 3 miles. Primary site contaminants are lead and zinc associated with the mining, beneficiation, smelting and refining of lead-zinc-silver ores. Lead smelting commenced in 1917 and zinc refining operations began in 1927. Operations ceased in 1981. Over the period of operation of these facilities, metals were emitted to the atmosphere from both point and fugitive sources. Tailings from the beneficiation operations were discharged to the Coeur d'Alene River prior to the construction and use of tailings impoundments. These emissions and discharges resulted in widespread contamination of area with metals (3).

The management of large, complex Superfund sites requires years of effort by many parties, and is composed of a series of individual projects and concurrent tasks. Each task requires development of its own quality assurance plan. Quality control within and between projects relating to the same site is an important element of an overall quality assurance program. Due to the size of the site (21 square miles), the number of parties involved, and the length of time until remediation is complete, the use of Site Comparison Samples (SCS) as tools for applied quality control allow quality assurance of data between projects on the same site.

As a result, two requirements presented themselves simultaneously:

(1) The need to develop large, homogenous volumes of heavily contaminated soils for treatability studies , and

(2) The need to develop large homogenous samples of soils which should be processed as Site Comparison Samples ("SCS project").

Field screening using FPXRF technology was selected as the analytical tool to ensure that appropriate soils were developed for both of these purposes.

FIELD ACTIVITIES

Over 500 kilograms of soil was required for the site studies and the SCS project. The soils needed to be heavily contaminated and as dry as possible. Authorization to proceed was received in October 1987. Then current weather conditions in northern Idaho were unusually dry for that time of year; hence, any field effort had to be mobilized quickly or postponed until the following summer. Postponement was not acceptable. The high cost of the treatability studies and the critical nature of the SCS project to the long term quality control program at the site demanded that soils of known concentrations with known data quality be obtained; sample collection without concurrent analysis was not acceptable. Field activities needed to be supported, therefore, with instrumentation that could be mobilized quickly, be portable enough to be moved throughout a large site and be capable of providing analytical responses to field personnel on a "real-time" basis.

Equipment

The FPXRF used at Bunker Hill is the X-Met 840 manufactured by Columbia Scientific Industries Corporation. A technical description highlighting its applicability for use at hazardous waste sites is provided by Piorek and Rhodes (4). The X-Met 840 is a self-contained, battery powered, microprocessor-based, multichannel X-ray fluorescence analyzer weighing 8.5 kg. The surface analysis probe is specially designed for field use. The X-Met 840 is hermetically sealed and can be decontaminated with soap and water. The probe includes a radioisotope source of Curium-244, a proportional counter and the associated electronics. The source is protected by an NRC-approved safety shutter.

The electronic unit has eight calibration memories called "models". Each model can be independently calibrated for as many as six elements each. These can be used to measure elements from aluminum up to uranium assuming two probes with the associated isotope sources are available. The unknown sample intensities are regressed against the calibration curves to yield concentrations. For the Bunker Hill site only lead and zinc were investigated and only two models were calibrated. Model 1 was calibrated from background up to 4980 mg/kg Pb and 9791 mg/kg Zn.

Reference Soil Standards for Quality Control and Standardization

The commercially available FPXRF systems use standards to establish calibration curves for comparison. Heretofore there has not been a demand for FPXRF systems in hazardous waste screening. Because of this low demand, there were no standards commercially available until recently. Columbia Scientific Industries Inc. (CSI) has produced the first set of commercially available standards designed specifically for hazardous wastes in soils. The primary calibration curves are based on these standards, which are listed in Table I as CSI. A description of a calibration technique for X-Ray Analyzers used in hazardous waste site screening is presented by Piorek and Rhodes (5).

Sampling

Sampling was completed in two days. Formerly acquired metals data was reviewed to identify several potential areas for field screening. These were visited in an attempt to limit the number of areas actually screened with the FPXRF. Three areas ranging in size from less than one to greater than 10 acres appeared to be appropriate, i.e., existing data suggested heavy contamination at those locations, the soil matrix was typical of the area, the areas were accessible and dry, and samples processing could be accomplished without disrupting other activities.

FPXRF screening was accomplished in two steps. First, a series of stations were staked and located on site maps. A two-person crew was used, one to set stakes and one to map the sample locations using a Brunton compass and a 300 foot tape. Second, a two-person FPXRF crew completed on site screening at each station. One person operated the instrument and one served as data recorder.

FPXRF data was acquired at each of the three target areas at a rate which exceeded one data point per two minutes. The rate limiting factor at each target area was the time required to survey the sampling grid, not to operate the FPXRF instrument. It might have been possible to eliminate the second person on the FPXRF crew without compromising the data acquisition rate. More time was required to move between target areas than to sample once the team was in an area. Typical FPXRF measurement times were 20 seconds per data point.

The levels of contamination as measured by the FPXRF for stations within the three areas ranged from 2300 to 70,000 mg/kg for lead, and 750 to 27,000 mg/kg for zinc. These values cannot be compared directly to contaminant values as obtained by standard SW 846 methods or CLP methods because they use partial digestions or extracts for analysis and FPXRF provides total elemental (or bulk) analyses.

Based on a review of these data, bulk soils were collected at two target areas between stations exhibiting the highest contamination levels. Sixteen samples, each with a field weight of at least 60 pounds was collected. Prior to shipping , each of these was analyzed in duplicate for lead and zinc by the FPXRF. Lead contamination in the samples ranged from 15,000 to 67,000 mg/kg. Zinc ranged from 1900 to 28,000 mg/kg. Samples with this level of contamination were adequate for both the SCS project and the treatability studies.

SCS DEVELOPMENT

As analytical instrumentation has moved into the field to complement laboratory instrumentation, so have the inherent problems of quality assurance and the application of field quality control to compare to data produced by established "conventional" methods of sample analysis. Given the problems of variability in results caused by selection of sampling points on a site, or by variability in relative large volume samples later analyzed by small aliquot "high sensitivity" methodologies, project officers and sample plan designers have turned to two recognized QC procedures to establish comparability; splitting samples between analytical facilities and increased use of Standard Reference Materials. With the increased use of contract laboratory facilities, the problems have increased disproportionately with each added analytical facility introduced in the larger multiple party sites.Cost and resource expenditure in time and logistics increase.

Definition

"A Site Comparison Sample (SCS) is a site specific reference material which is representative of the type of problems encountered when analyzing or treating materials from the site." SCS's:

- Contain key contaminants in the matrix of the site;
- Are available in sufficient numbers to satisfy numerous site management and QA/QC purposes;
- Exhibit the lowest possible coefficient of variation (cv);
- Are managed by an organization capable of being a depository of analytical results, providing a common management point for quality assurance, inter- and intra-laboratory studies.

SCS differ from Standard Reference Materials (SRM) by virtue of being site specific, and not produced under a protocol requiring the pre-release rigorous analytical method specific, statistically validated characterization applied to SRMs. They also differ from Performance Evaluation (PE) samples used in studies to directly compare inter-laboratory results under a defined methodology. A SCS stock could conceivably provide the material for a SRM or PE, but would require those protocols to be applied before so identifying.

Quality assurance of data developed from multiple sources presents a complex situation. One major problem is the question of sample variability and comparability caused by distribution of compounds of interest on a site. A second is the variability inherent in, and between, analytical methods, particularly due to matrix interference effects. Two common techniques for dealing with these problems are the use of "split" samples and analyses of Standard Reference Materials. Splitting increases the risk of magnifying the problem due to distribution; standard reference materials seldom reflect the matrix effects present in "natural" site samples.

Late in 1984 and early in 1985, the concept of manufacturing a homogenized bulk sample was developed to provide vendors of propietary soil stabilization services uniform materials for evaluation. The use of screening techniques to define areas of concern on a site was directly applied to statistically choosing sources of material to provide a sample representative of the more highly contaminated material distributed in the matrix of the site. Mixing methods were investigated from the viewpoints of cost, available resources, and practicality. Separate elements of the methodology were tested on available materials at various sites. Protocols and standard operating procedures regarding from where to select the material, how to homogenize it, and how to fill the bulk sample containers in a manner that would reduce bias in the distribution of the material to the large bulk containers were developed.

The question of how to mix bulk samples of site matrix materials to achieve a relatively homogenized material had to be answered empirically. Because of the wide variety of particle sizes, moisture content, cohesive characteristics and distribution of contaminants, it was decided to thoroughly mix the material for the first 1400 pound sample by manually quarter piling through several cycles; and then do a multiple random fill of enough buckets (sixty-nine) to meet all projected needs. It was labor intensive, and took 4 people most of one day.

The sequence of events discussed in the creation of the bulk reference materials led logically to the concept of further treatment of the bulk material to provide a "Site Comparison Sample (SCS)" for each major site. Initially, approximately two dozen 8 oz. sample containers were "broken out" of a bucket, and used for comparative analyses to determine the degree of mixing achieved. Some pressure was felt to supply some of these for comparison analyses instead of splitting samples. At that time, resources were not available to so use the material; no statistically sound evaluation of the material existed to back up any results.

It cannot be emphasized too heavily that the SCS is not be to considered a sample that represents the actual concentration of a contaminant at any given point on a site. Also, it cannot initially be considered as a true SRM, although it may be possible to up-grade it's status if a large number of SCS are generated, and enough analytical resources are available to utilize a portion of the banked samples for a statistically sound standardization analyses. The concept of the SCS is to produce a material that can be used in lieu of split samples, and provide a data bank for both continuing and retroactive analysis of variation due to differing methods of sample acquisition, handling, and analyses. As the discrete SCS will be archived in controlled storage, the effects of holding time can be demonstrated for each set by continuing characterization analyses. The more SCS analyzed, the stronger the statistical evaluation of all data generated by analyses becomes; not only of the SCS bank itself, but of the sample of record data and the laboratories producing the data.

In Statistics there is the "The Central Limit Theorom": It states:

> "From an unknown distribution a random sample size n is obtained. If n is allowed to become larger, the sample mean will behave as if it came from a Normal distribution, regardless of what the parent distribution looked like."

John Webber, Statistician for EPA Office of Policy and Planning, had provided a table illustrating how Normality affects a sample population (Table II) taken from a universe, and reverse logic suggests that very low variances could be expected from discrete samples of n_h, especially if the discrete samples were produced by actually filling the randomly selected sample containers with a series of multiple portions selected at random from the bulk n_h material. (The "double random" referred to hereafter.)

Reasoning from this point, if n is sufficiently large, and then thoroughly mixed or homogenized, multiple random creation of n_h should result in a low variance that approaches the "true" value of the concentration of the mean of n. As the number of random selections used to create n_h increases, the coefficient of variation should decrease.

Through the balance of 1985 and into 1986, the analytical results from the stabilization tests made on the bulk materials were reviewed Protocols were developed through experimentation to mix sludges of water, sediment and hydrocarbon products. A protocol for groundwater SCSs was developed

Finally, in late 1986 an opportunity presented itself to produce an actual SCS for a large, established Superfund site. This dovetailed with the trial of the X-Met FPXRF equipment, and made it possible to more soundly screen the bulk "raw material" for both stabilization studies and two SCSs; one "high" range and one "low" range. A fairly ambitious design was proposed to produce between 300 and 500 8 oz. samples in each range.

Experience with the homogenization of the original stability samples suggested that it would be desirable to utilize more efficient methods of mixing the bulk sample material. Accordingly, a "drum roller" was obtained, and 55 gal O.T. steel drums were modified with two interior deflection vanes similar to those used in industrial dry mixing of materials. The bulk sample material was batched through this drum and then spread out in a distribution box for the double random selection of the SCS samples. The available quantity of material dictated that only a single SCS be produced, so the "high" and "low" bulk retains were incorporated into a single batch for processing.

The 600 aliquots have been "banked", and a master random distribution list prepared. From the bank, an initial set of 10 SCS (the first block on the list) were supplied to the USEPA Environmental Monitoring Services Laboratory, Las Vegas, NV. for preliminary characterization analyses. At the same time, a principle contractor was issued the next 30 samples for release to their contract laboratories for the same purpose. All analytical data results are to be reported to Region 10, and a running control chart of results developed.

As the number of samples analyzed increases, the data will become progressively more refined, and amenable to other statistical analyses to more closely define the sources of variability, from laboratory, to method, and to a certain extent, the effects of holding time. Data currently available are presented in Figures 1 and 2. Although the number of data points are limited, there is a suggestion that inter-laboratory differences may be important (Figure 1), and that overall cv's are low (less than 30%).

As related, this is an ongoing developmental effort. Preliminary data indicate the approach is sound. For middle to large site hazardous waste operations, and for long term ambient monitoring projects, the economies of scale would apply. For improved data quality and scientific credibility the concept is entirely appropriate and defensible. The practical application awaits resources and initiatives on the part of the user programs.

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(3) .Gulf Resources and Chemical Corporation, "Bunker Hill Site Remedial Investigation/Feasibility Study for Unpopulated Areas," April 24, 1987.

(4) Piorek, S., Rhodes, J. R., "Hazardous Waste Screening Using a Portable X-ray Analyzer," Symposium on Waste Minimization and Environmental Programs within DOD, American Defense Preparedness Association, Long Beach, California, April 1987.

(5) Piorek, S., Rhodes, J. R., "A New Calibration Technique for X-Ray Analyzers Used in Hazardous Waste Screening"

Table I

Concentrations of Standards

(All values are in mg/kg)

	Standard Elements: Name	Pb	Zn	Cu	As
1	CSI 1B	0	4790	4790	6970
2	CSI 2B	0	0	0	11,340
3	CSI 3B	4980	0	0	0
4	CSI 5B	240	240	8160	7740
5	CSI 6B	484	482	6300	5590
6	CSI 7B	4760	4900	3810	11,070
7	CSI 8B	1474	983	2950	4530
8	CSI 9B	1990	2970	982	3390
9	CSI 10B	2930	3910	1960	2250
10	CSI 11B	2440	6360	490	1140
11	CSI 12B	3405	8270	243	565
12	CSI 13B	4126	9791	96	224
13	CSI 14B	0	0	4950	0
14	CSI 15B	0	4950	0	0

Table II

Illustration of How Normality Affects Samples

Let us phrase the question "How many samples do I need to be within Q sigma "s" (Standard Deviations) of the true value?":

	Confidence 90%		Confidence 95%		Confidence 99%	
Q Sigma "s"	Normal	Worst Case	Normal	Worst Case	Normal	Worst Case
2s	1	3	1	5	2	25
1s	3	10	4	20	6	100
0.75s	5	18	7	36	10	178
0.5s	11	40	16	80	22	400
0.4s	17	63	25	125	34	625
0.3s	31	112	43	223	61	1112
0.2s	68	250	97	500	136	2500
0.1s	271	1000	385	2000	543	10000

from: "Statistical Considerations in Sampling Hazardous Waste Sites", John Warren, E.P.A./O.P.R.M.

Figure 1

BETWEEN LABORATORY COMPARISON

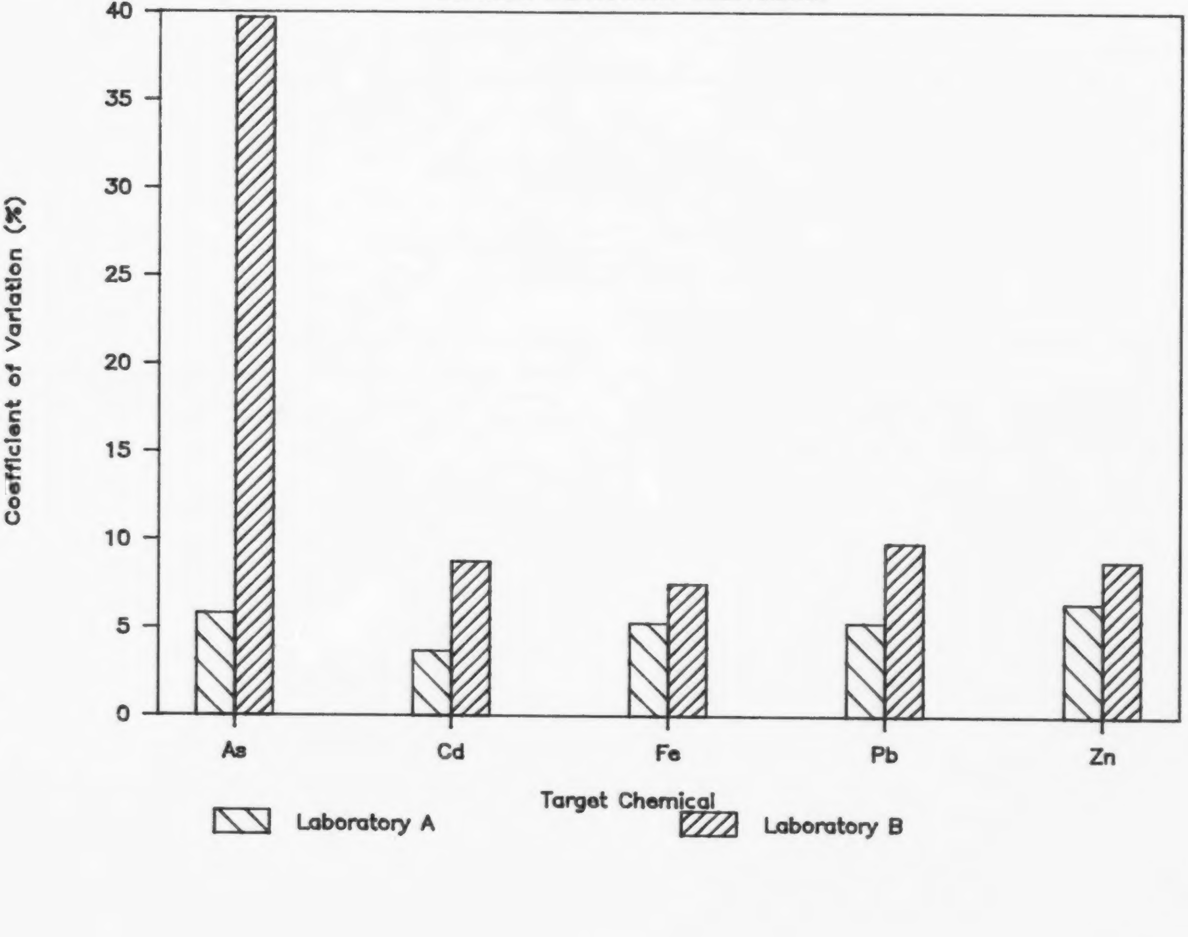
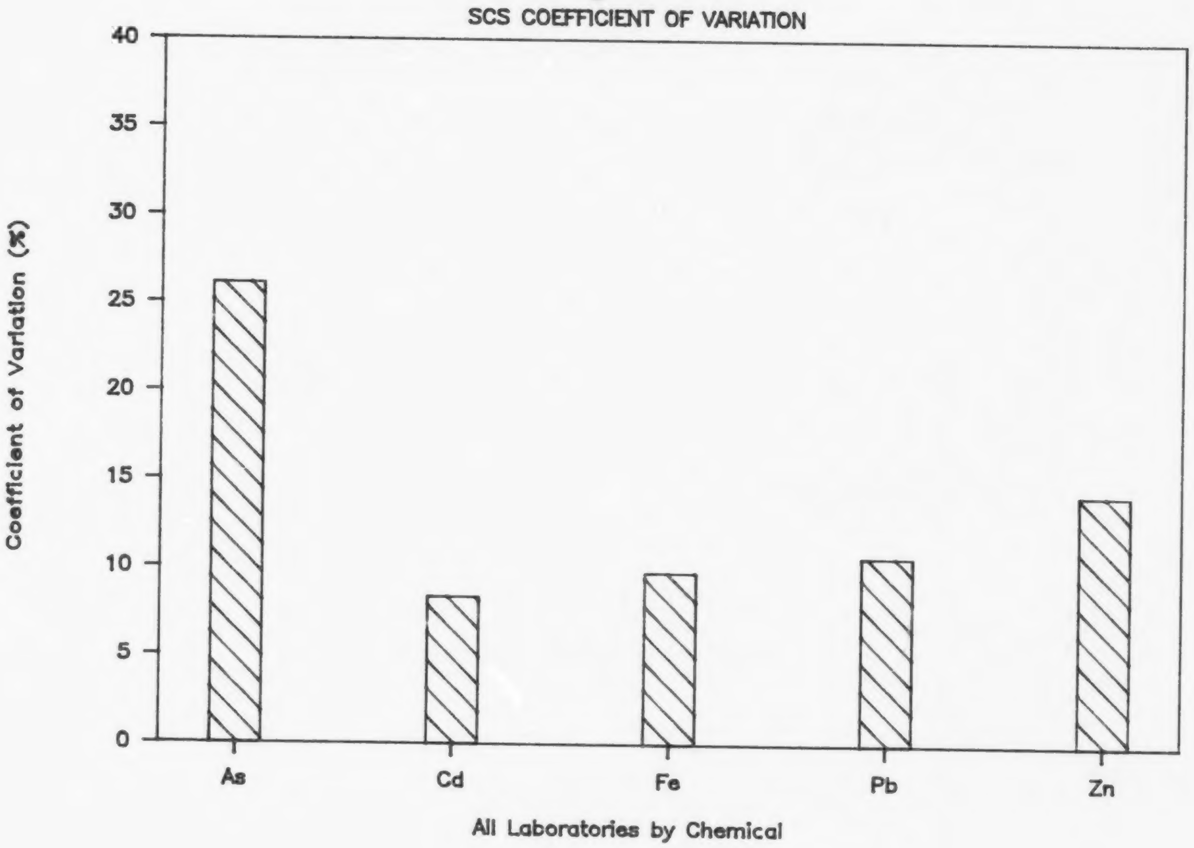


Figure 2



DISCUSSION

HAROLD VINCENT: How were you going to apply the zeolites to the problem?

JOHN BARICH: Our first step was to determine whether or not the zeolites would be a useful soil amendment. If the answer to that was a strong yes, then the application technique would have been the next thing we would have looked at.

HAROLD VINCENT: That's in place of removal?

JOHN BARICH: In place of removal, yes. We had literally many square miles of land whose condition needed to be improved. There was just not enough secure landfill capacity, to do anything other than *in situ*.

LOW LEVEL XRF SCREENING ANALYSIS
OF HAZARDOUS WASTE SITES

Randy Perlis
Mark Chapin
Ecology and Environment, Inc.
Denver, Colorado

ABSTRACT

Recent field investigations have demonstrated the successful use of XRF screening analysis for metal contamination at various hazardous waste sites.

Using minimal sample preparation and field sampling methods the results were comparable to laboratory results using conventional methods such as AA and ICP. Multi-elemental analysis was performed on soil samples with particular interest in lead, arsenic, chromium, and copper levels. Detection limits achieved for some elements were 10 ppm. The XRF inorganic results were used in mapping and contouring the extent of contamination of a hazardous waste site containing organic and inorganic contamination.

The lower detection limits and quick turn around times proved the feasibility of the XRF in screening of hazardous waste sites and environmental monitoring.

INTRODUCTION

The Ecology and Environment, Inc. (E & E) Field Investigation Team (FIT) was tasked by the U.S. Environmental Protection Agency to initiate a field analytical screening program (FASP) to assist in site investigations and listing or expanded site investigations. Field screening is projected to enhance the pre-remedial program by: 1) assisting the EPA in completing the site inspection inventory in a timely manner, 2) decreasing the number of "non-detected" samples, 3) supporting the revised Hazardous Ranking System, and 4) accelerating scope of remedial investigations and feasibility studies. The increased sampling capability consequently increases the chances of detecting a release without compromising data quality, since rapid turn-around of screening samples allows selected split sample Contract Laboratory confirmation. Part of this program was to develop a screening analysis for metal contaminated solids such as soils and sediments including mine tailings and mining waste materials in EPA Region VIII. FIT determined the best instrumentation for these types of analyses would be an x-ray fluorescence spectrometer (XRF). Previous successful operations with the XRF (Raab et al, 1987; Furst & Spittler, 1985; Mernitz & Staible, 1985; Piorek & Rhodes, 1987) indicated the XRF's usefulness in screening analysis of metal contaminated solids on potential hazardous waste sites. However, lower detection limits below 100-200 ppm were difficult to achieve.

The rapid turn around times available on a wide variety of elements and minimal sample preparation made the XRF almost ideal for screening analysis. As previously stated, one of the major drawbacks associated with the XRF was the relatively high detection limits. However with the Tracor 6000 XRF, E & E is able to achieve detection limits of 10 parts per million consistently and confidently without liquid nitrogen cooling of the XRF detector as needed for other conventional low level XRF analyses. This advantage greatly increases the mobility of the instrument. These detection limits are more than adequate for most soil samples from metal contaminated sites.

The purpose of this paper is to summarize E & E's experience with low level XRF analysis to date and present the comparability of data of XRF screening analysis and AA/ICP analysis from the Contract Laboratory Program on co-located samples. An example of how the XRF screening analysis is used to characterize a hazardous waste site with grid sampling and contour mapping is presented.

This material has been funded wholly or in part by the United States Environmental Protection Agency under contract #68-01-7347 to Ecology and Environment, Inc. It has been subject to the Agency's review, and has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INSTRUMENTATION

The Tracor Spectrace 6000 energy dispersive x-ray fluorescence analyzer system includes the following specifications. The source is a 50KV, 0.35mA rhodium x-ray tube. The unit has two available filter positions with a 0.13mm aluminum filter and a 0.13mm rhodium filter. Also used is a 0.13mm copper filter. The x-rays are filter directed. The detector is a thermally cooled (Peltier) detector with a 20 square millimeter area. The detector is cooled to approximately -76 degrees C. The analyzer is a multi-channel analyzer with 1024 channels. The XRF unit is controlled by a NEC Power-Mate II P.C. that controls the spectrometer and receives the data via an interface card in the P.C.

The lower detection limits are achieved on this XRF unit due to the high flux x-ray tube, thermally cooled high resolution detector, and peak deconvolution software. Earlier XRF instrumentation work was done with instruments using radioisotope source (low resolution) excitation and low resolution proportional counter detectors. The Peltier cooled detector exhibits relatively little performance differences compared to liquid nitrogen cooled detectors (Harding, 1988).

XRF OPERATION

Elemental identification and quantitation is obtained using the "Fundamental Parameters" PC software (PCXRF) integrated with the Tracor 6000 XRF (Leyden, 1984).

When elements present in a soil sample are irradiated with a beam of x-rays, electrons in the atoms lower lying energy levels are excited to higher energy levels. The vacancies left in the inner electron orbitals make the atom unstable. Relaxation to the stable ground state occur resulting in the emission of x-rays characteristic of the excited elements (Figure 3). Thus, by examining the energies of the x-rays emitted by the irradiated soil sample, identification of elements present in the sample is possible. Comparing the intensities of the x-rays emitted from a given unknown sample to those emitted from reference standards with known analyte concentrations allows quantitation of the elements present in the sample.

During sample analysis a spectrum is acquired as shown in Figure 1. Optimized for various emission energy levels with different instrumental parameters and excitation conditions the XRF is able to analyze for various elements. Generally, elements are segregated for analysis into groups having similar atomic numbers. Currently we are analyzing for fourteen different elements using three separate excitation conditions. Figure 1 is a sample spectrum for the high atomic number elements: manganese, iron, nickel, copper, zinc, arsenic, and lead. Figure 2 is identical to Figure 1, but has the mid atomic number elements analysis superimposed on to it. Elements of interest here include potassium, calcium, and chromium. The superimposed spectrum shows that the excitation conditions employed for the mid-atomic number analysis greatly enhance the spectrum for those elements. As previously stated, peak position along the spectral energy axis (horizontal axis) is indicative of the metal it arose from, and is therefore the primary basis of elemental identification. It should be noted that each metal will exhibit several peaks in the spectrum, since a separate peak will be observed for each allowed electron orbital energy transition. For example, peak A in Figure 1 is lead's L-alpha line. It arises when electrons initially excited to a lead atom's M shell return to the lead atom's L shell giving off x-rays which have an energy of 10.5 KeV. Peak B is lead's K-beta line. When electrons in the lead atom energetically relax from the N shell to the L shell, x-rays at 12.6 KeV are emitted. Figure 3 shows a representation of this process.

The multiple linear least squares deconvolution that is used is excellent method of unfolding peak overlaps in a spectrum. The software peak extraction routine can integrate any emisison line in the spectrum.

Prior to running a series of samples, the instrument is calibrated using a pure copper disk. Basically, the instrument adjusts its spectral energy axis until the copper x-ray emission peaks fall at the correct energies. The energies of other metal peaks are then determined relative to the established copper peaks. This peak position monitoring is performed at least daily.

The area under each element's peaks, termed peak intensity, is proportional to the concentration of that element in a sample. Through peak deconvolution and using multiple linear least squares, integration is carried out and the results evaluated using Tracor's "Fundamentals Parameters" software (Leyden, 1984 and Leyden, 1988).

XRF STANDARDIZATION

Standardization in the PCXRF program, which is propriety fundamental parameters routine that is integrated into the SSXRF software that controls the spectrometer functions, is computationally complex but descriptively quite simple. The PCXRF program proceeds by modeling the x-ray tube output from the spectrometer and using fundamental parameters, the standard concentrations, and the measured intensities for the standards to calculate pure element count rates for the XRF measurable elements. Theoretical standards are produced solely to compute alpha coefficients which account for all matrix interactions. The pure element count rates and alphas on stored on disk.

To compute unknown concentrations, an estimate of concentration is first made using the pure element count rates and measured peak intensities for the unknown. This is followed by a calculation of expected intensities from the predicted composition of the unknown and the alpha coefficients. These new computed intensities are compared to the measured intensities and in light of the result, a new approximate composition is assumed. The iteration proceeds through composition/expected verses measured intensity/new approximation of composition. If the two compositions disagree by less than 1%, convergence is assumed and the final composition is output as the result for the unknown (Harding, 1988).

For initial standardization, a set of reference standards with known analyte concentrations is run. Currently, certified samples are available from the U.S. National Bureau of Standards and Canadian Certified Standards Center. These certified standards are very well characterized and employ up to seven different analytical methods. In a typical XRF analysis the standards are used to construct a calibration curve by plotting measured x-ray intensities against known concentrations. However, in soil sample analysis, the varied composition of the soils causes problems that can attenuate the emissions from elements being analyzed. In general, the absorbing properties of a soil matrix, termed matrix effects, increase as a function of the average number of the elements in the sample increase. In addition to matrix effects, there are inter-elemental effects. Inter-element effects occur when an element in the matrix can specifically absorb or enhance x-ray photons emitted from another element. The "Fundamental Parameters" program quantitatively corrects for changes in the sample's matrix and for inter-element effects (Criss & Birk 1986, 1978; Leyden 1984, 1988).

QA/QC

QA/QC for XRF screening analysis includes duplicate samples, standard checks, and splits with other laboratories. Sample duplicates are run at a 10-20% frequency with the smaple split before sample preparation. This will indicate the precision of an analysis as well as the homogeneity of the sample matrix.

National Bureau of Standards (NBS) or Canadian Certified standards are run at a 10-20% frequency to determine continued standardization of the instrument.

Also splits of the solid sample materials are sent to analytical laboratories for AA/ICP comparison at a 10-20% frequency rate.

SAMPLE PREPARATION

Soil and sediment samples are collected with the usual protocol, however not as large a sample is required as with the acid digestion AA/ICP analyses. However, the most homogeneous sample possible is recommended.

No great differences have appeared as whether grab or composite sampling is more suitable provided the samples are well mixed. Grab samples have shown a slight statistical advantage in comparing with AA/ICP results.

Analysis of particulates collected on dust filters is just now being tested. No sample preparation is involved with air filters, however accuracy of the results depends greatly on sampling procedures and accurate measurement of the amount of particulate matter collected.

Sample preparation for XRF screening analysis was designed to be kept simple. XRF sample preparation procedures can be as complex as pellet pressing or fluxing the sample. Accuracy of XRF results and their relation to sample preparation is described in detail by Wheeler, 1987. However XRF sample preparation procedures are still obviously quicker and less hazardous than the acid digestion AA/ICP methods.

The XRF screening sample preparation is minimal to ensure rapid turn around. This sample preparation includes air or mild oven drying of the solid sample and mixing in a mortar and pestle to homogenize the sample as much as possible. No sieving is performed unless the sample contains particles larger than 10 mesh.

COMPARISON OF RESULTS

As in any inter-method comparison, the more alike the sample and the procedures, the more valid the comparison. However, in dealing with soils and solid matrix contaminants, the homogeneity of the sample is always in question and therefore a true duplicate or split is extremely difficult to obtain. Also, comparing a XRF method with an acid digestion AA/ICP method is risky since both methods (including standardization and sample size) are quite different.

Since most comparisons are used beyond the intent of the initial project, one must keep in mind we are comparing AA/ICP litigation and regulatory enforcement CLP data with XRF screening data.

Figures 4,5,6, and 7 represent comparisons of chromium, arsenic, copper, and lead XRF results with typical AA/ICP laboratory results (SW-846). Lead and copper comparisons had excellent correlation coefficients of 0.97 and 0.98 respectively. Arsenic's correlation coefficient was 0.89. However three outlier points are noted and therefore the actual correlation may be better than reported. The correlation coefficient for chromium was 0.81. Chromium appears to be biased high on all XRF results. The relatively low correlation can be attributed to the low measured intensities of the chromium in the standard materials, hence the accuracy with which pure element count rates can be calculated is poor.

All XRF results appear to be biased high compared to the AA/ICP results. No documented explanation is available at this time to explain this, however current speculation attributes this occurrence to the AA/ICP acid digestion procedure, the total sample analysis with the XRF, standardization procedures, and sample size.

INTERPRETATION OF RESULTS

Sampling points or grid layouts are critical for proper interpretation of the XRF results. Usual grid layouts are based on site size, detail of investigation, turn around time, and economics such as number of samples and man hours available.

Interpretation of XRF results should be restricted to use for evaluation and assessing the results for average pollutant exposure to humans and animals. This level of analytical requirements should show a precision of 10% and an accuracy of 15% on samples in the calibration range of the instrument.

The majority of XRF samples are run for field screening purposes at lower analytical requirements and the results are used for screening, preliminary evaluation, and on-site decision making.

The figures presented show contamination zones and relative amounts of contaminants of a hazardous waste site. The intensity of the sampling was employed to characterize the waste present on the site and in the immediate areas and to evaluate the on-site direct contact pathway. The contouring program employed was the Kriging contour method. Figures 8-15 present results of a grid examination of a site using XRF analysis. Figures 8 and 9 show overlays of the contouring with the site map. Figure 8 represents the zinc contouring while Figure 9 represents the lead contamination. The comparisons of these contour maps shows that lead and zinc high contamination zones are not related and the contaminaiton extends beyond the site's boundaries. Figures 10,12, and 14 show the grid layout of the site for different elements with contouring. Figure 10 represents a more detailed contour of the lead contamination as compared to Figure 9. Figure 10's data points have the actual XRF concentration values in ppm printed above the points. Comparing Figures 10,12, and 14 (lead, arsenic, and copper), the contour maps show differing "hot spots" for each element indicating the independent variables involved at this site. Figures 11,13 and 15 show a three dimensional contouring of the various elements. Comparisons of the 3-D figures again reinforces the variability of the contamination zones and graphically illustrates the degree of contamination.

CONCLUSIONS

XRF screening analysis of low level metal contamination is proving to be valuable in the investigations of hazardous waste sites. XRF screening analyses have been proven very effective in establishing contamination boundaries using contouring maps and very useful in visualizing contaminated zones and amount of contaminants in comparision with background samples and on-site contamination. The cost savings compared to usual inorganic analytical services is estimated to be $80 per sample after instrument payoff. The turn around times with the XRF are conducive to field screening analysis. The small amound of sample necessary and minimal sample preparations diminishes health and safety problems and reduces the amount of sample disposal. With the advancing technology EDXRFs are becoming more mobile while maintaining low detection limits, thus field screening analyses are possible. Finally, the results obtained from XRF screening analyses show good correlations with other types of inorganic analyses and basic trends and comparisons can be confidently made.

ACKNOWLEDGEMENTS

The authors wish to recognize individuals who contributed to this paper. We thank Les Sprenger of the Region 8 EPA, Stuart Richardson and Karl Ford of Ecology and Environment, Inc., for providing the support and resources for this project. Greg Raab, LEMSCO, and Hunt Chapman, E & E, for review comments. Also Anthony Harding, Tracor X-Ray, Inc., for invaluable help in technical accuracy.

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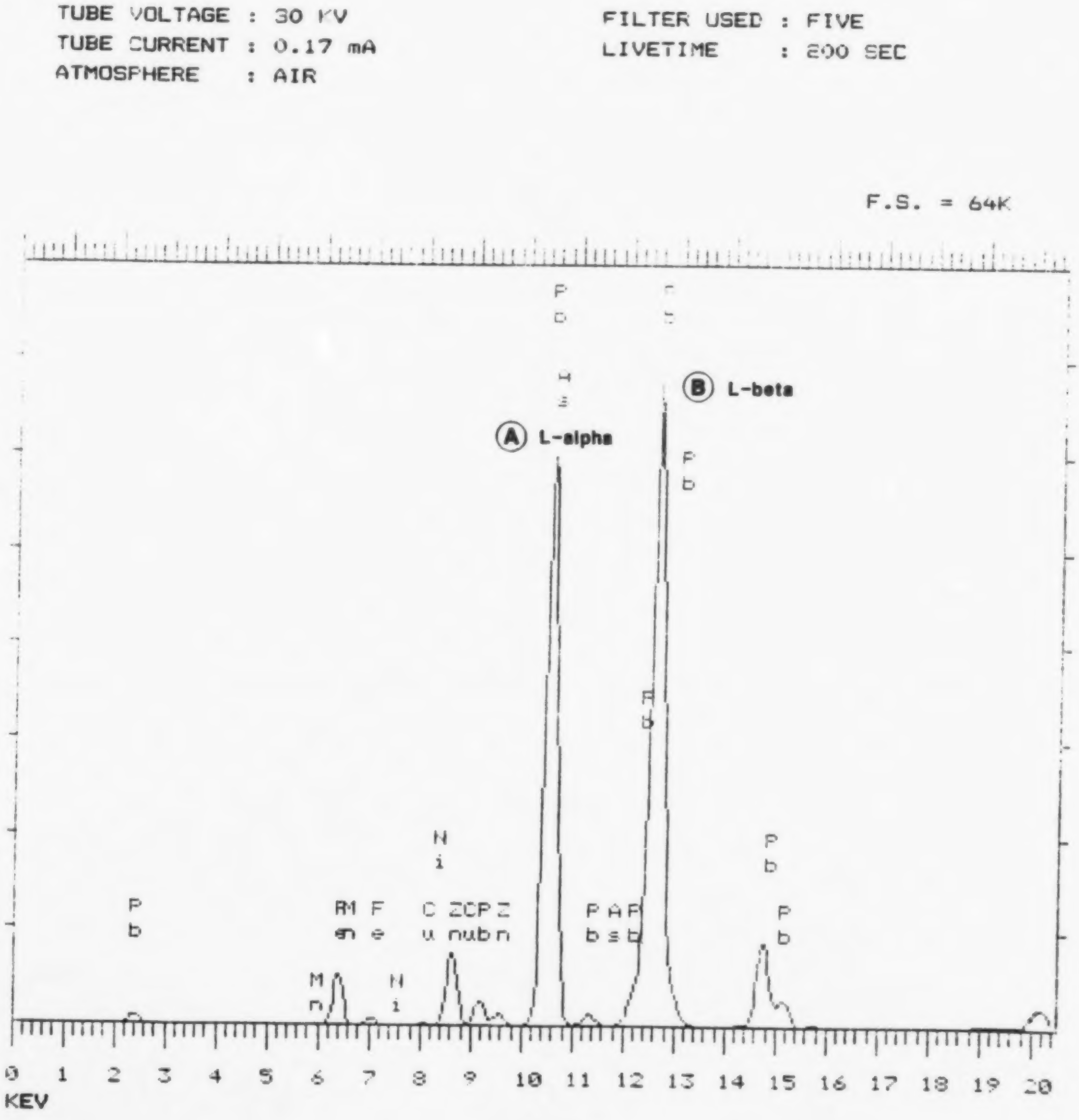


TUBE VOLTAGE : 30 KV
TUBE CURRENT : 0.17 mA
ATMOSPHERE : AIR
FILTER USED : FIVE
LIVETIME : 200 SEC

Figure 1

TUBE VOLTAGE : 30 KV
TUBE CURRENT : 0.17 mA
ATMOSPHERE : AIR

FILTER USED : FIVE
LIVETIME : 200 SEC

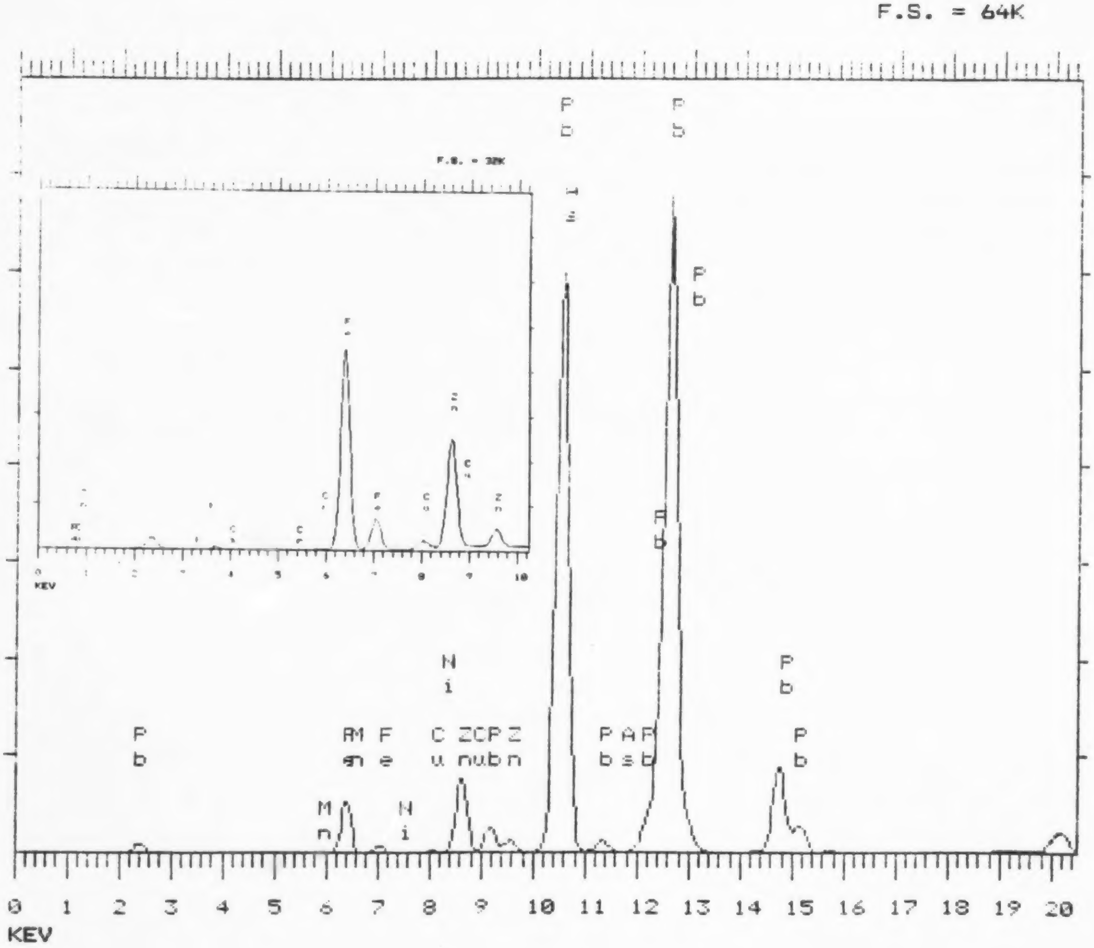
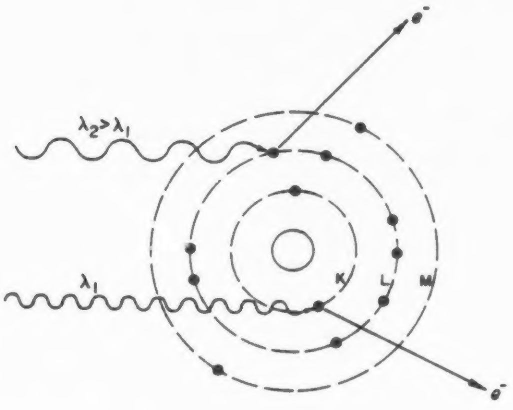
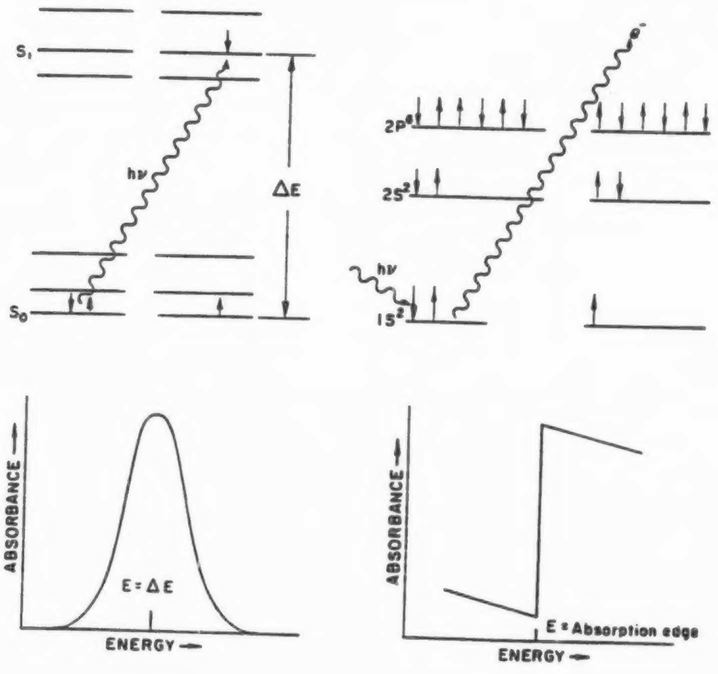


Figure 2


e^-
$\lambda_2 > \lambda_1$
λ_1
K
L
M
e^-

– *Illustration of photoejection of K electrons by higher energy radiation, and L electrons by lower energy radiation.*


S_1
hν
ΔE
S_0
e^-
$2P^6$
$2S^2$
hν
$1S^2$
ABSORBANCE
E = ΔE
ENERGY
ABSORBANCE
E = Absorption edge
ENERGY

A

B

– *Excitation of electron energy levels: (a) transition between two quantized energy levels and (b) photoejection of electrons by x-radiation*

Figure 3

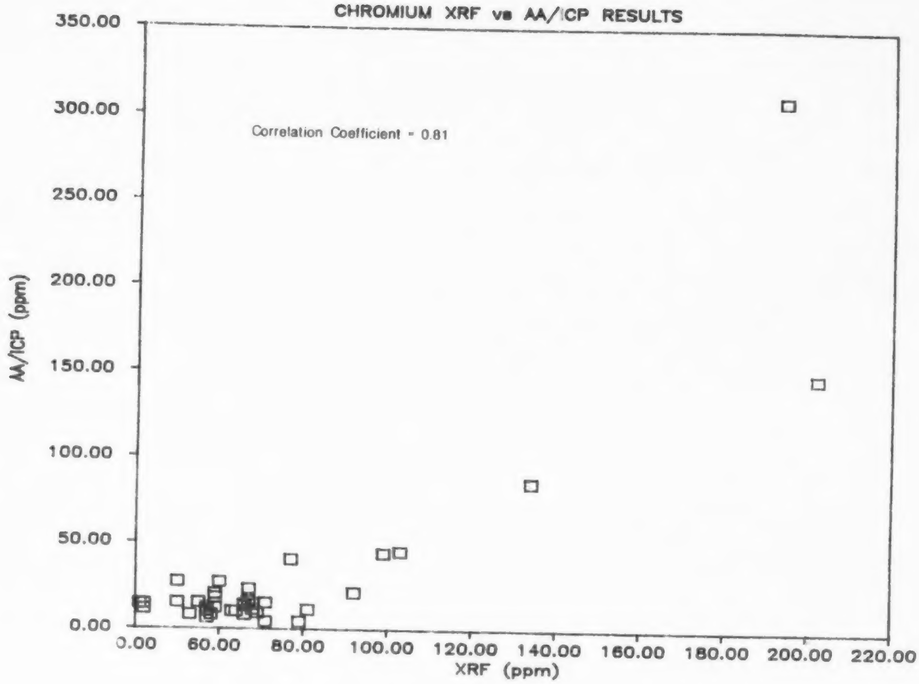


Figure 4

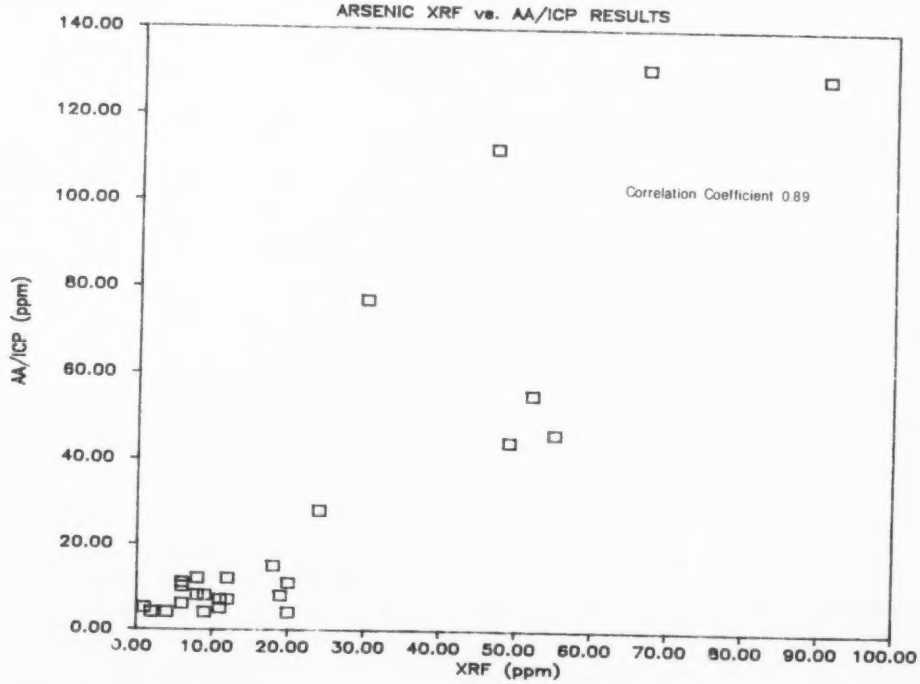


Figure 5

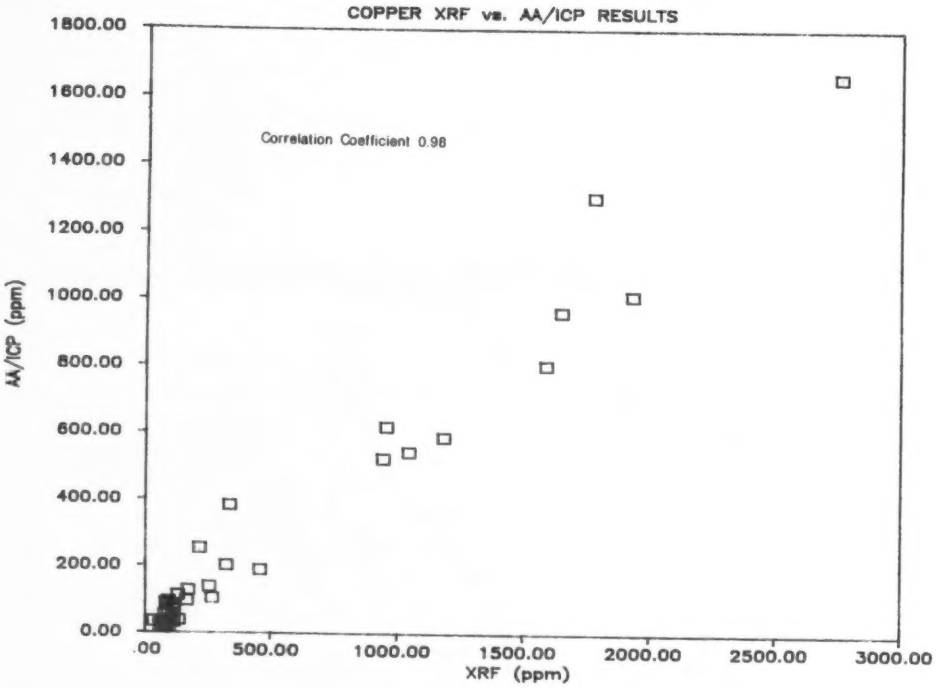


Figure 6

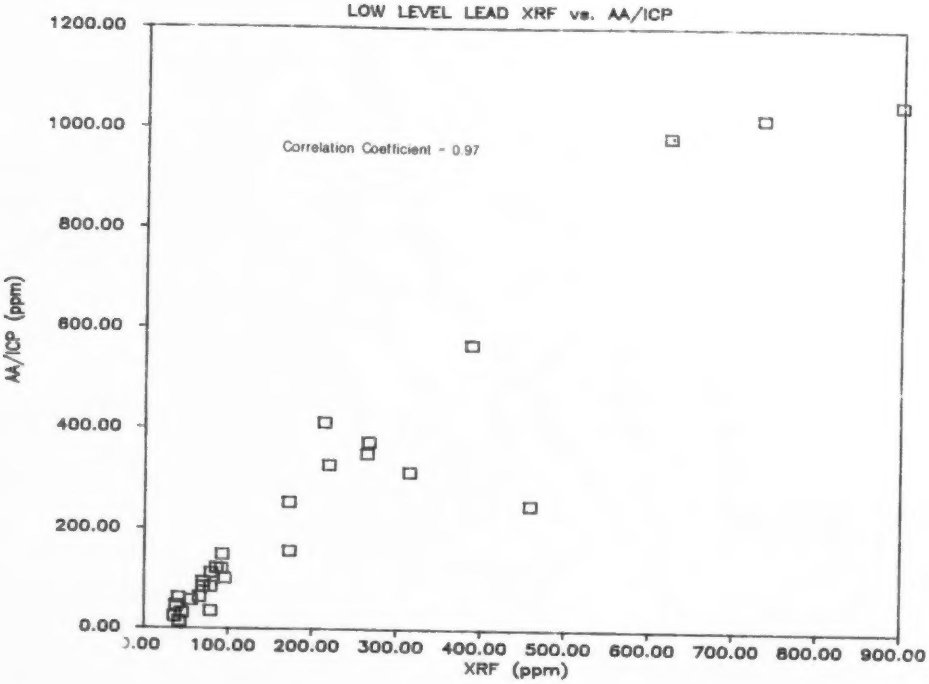
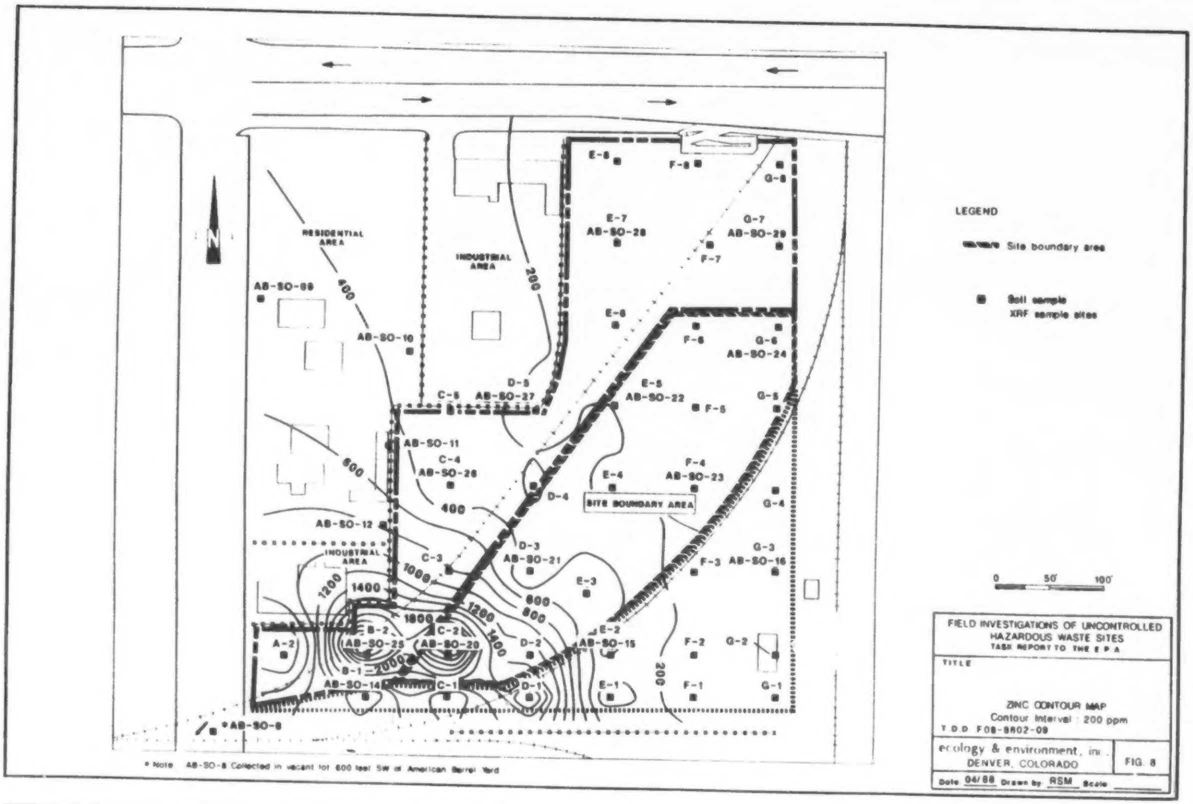


Figure 7


N
RESIDENTIAL AREA
INDUSTRIAL AREA
SITE BOUNDARY AREA
AB-SO-09
AB-SO-10
AB-SO-11
AB-SO-12
AB-SO-14
AB-SO-15
AB-SO-16
AB-SO-20
AB-SO-21
AB-SO-22
AB-SO-23
AB-SO-24
AB-SO-25
AB-SO-26
AB-SO-27
AB-SO-28
AB-SO-29
AB-SO-8
A-2
B-1
B-2
C-1
C-2
C-3
C-4
C-5
D-1
D-2
D-3
D-4
D-5
E-1
E-2
E-3
E-4
E-5
E-6
E-7
E-8
F-1
F-2
F-3
F-4
F-5
F-6
F-7
F-8
G-1
G-2
G-3
G-4
G-5
G-6
G-7
G-8
200
400
600
800
1000
1200
1400
1600
2000
LEGEND
Site boundary area
Soil sample
XRF sample sites
0
50'
100'

* Note AB-SO-8 Collected in vacant lot 600 feet SW of American Barrel Yard

FIELD INVESTIGATIONS OF UNCONTROLLED HAZARDOUS WASTE SITES
TASK REPORT TO THE E.P.A.

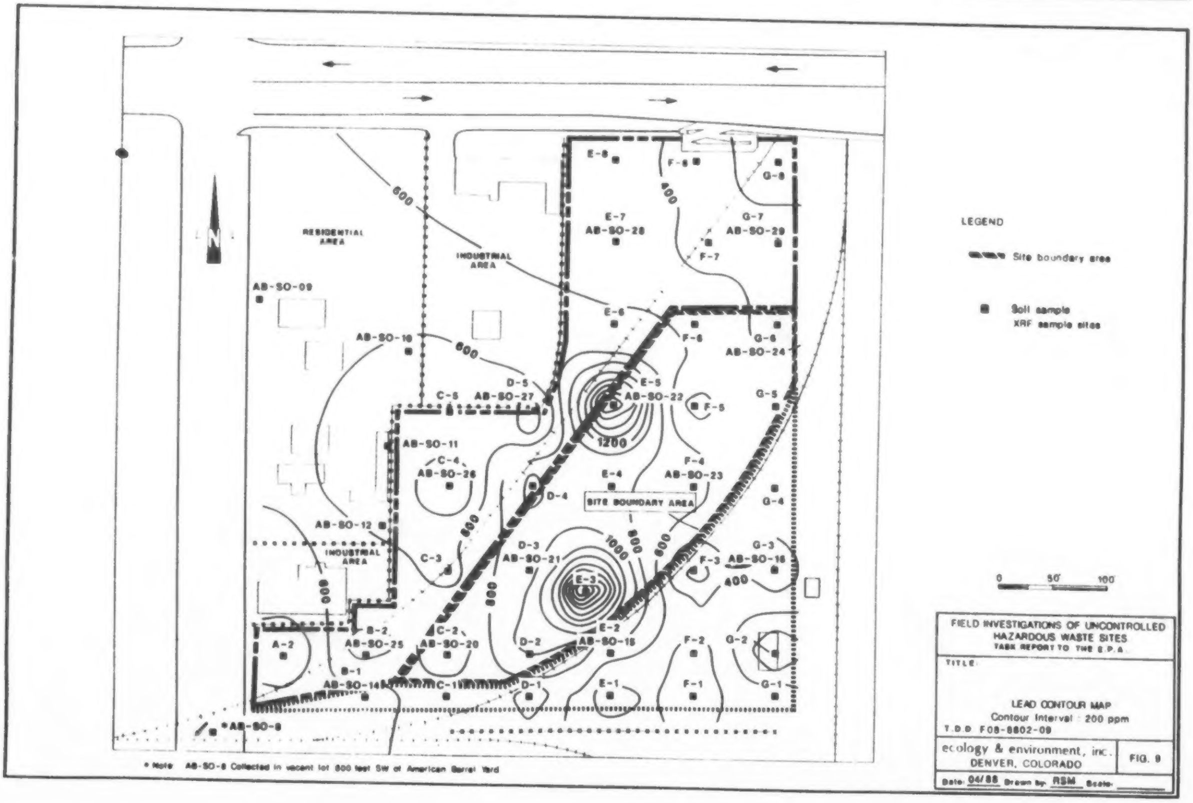
TITLE

ZINC CONTOUR MAP
Contour Interval : 200 ppm
T.D.D. F08-8802-09

ecology & environment, inc.
DENVER, COLORADO

FIG. 8

Date 04/88 Drawn by RSM Scale


N
RESIDENTIAL AREA
INDUSTRIAL AREA
SITE BOUNDARY AREA
AB-SO-09
AB-SO-10
AB-SO-11
AB-SO-12
AB-SO-14
AB-SO-15
AB-SO-16
AB-SO-20
AB-SO-21
AB-SO-22
AB-SO-23
AB-SO-24
AB-SO-25
AB-SO-26
AB-SO-27
AB-SO-28
AB-SO-29
AB-SO-8
A-2
B-1
B-2
C-1
C-2
C-3
C-4
C-5
D-1
D-2
D-3
D-4
D-5
E-1
E-2
E-3
E-4
E-5
E-6
E-7
E-8
F-1
F-2
F-3
F-4
F-5
F-6
F-7
F-8
G-1
G-2
G-3
G-4
G-5
G-6
G-7
G-8
400
600
800
1000
1200
LEGEND
Site boundary area
Soil sample
XRF sample sites
0
50'
100'

* Note AB-SO-8 Collected in vacant lot 600 feet SW of American Barrel Yard

FIELD INVESTIGATIONS OF UNCONTROLLED HAZARDOUS WASTE SITES
TASK REPORT TO THE E.P.A.

TITLE:

LEAD CONTOUR MAP
Contour Interval : 200 ppm
T.D.D. F08-8802-09

ecology & environment, inc.
DENVER, COLORADO

FIG. 9

Date: 04/88 Drawn by: RSM Scale:

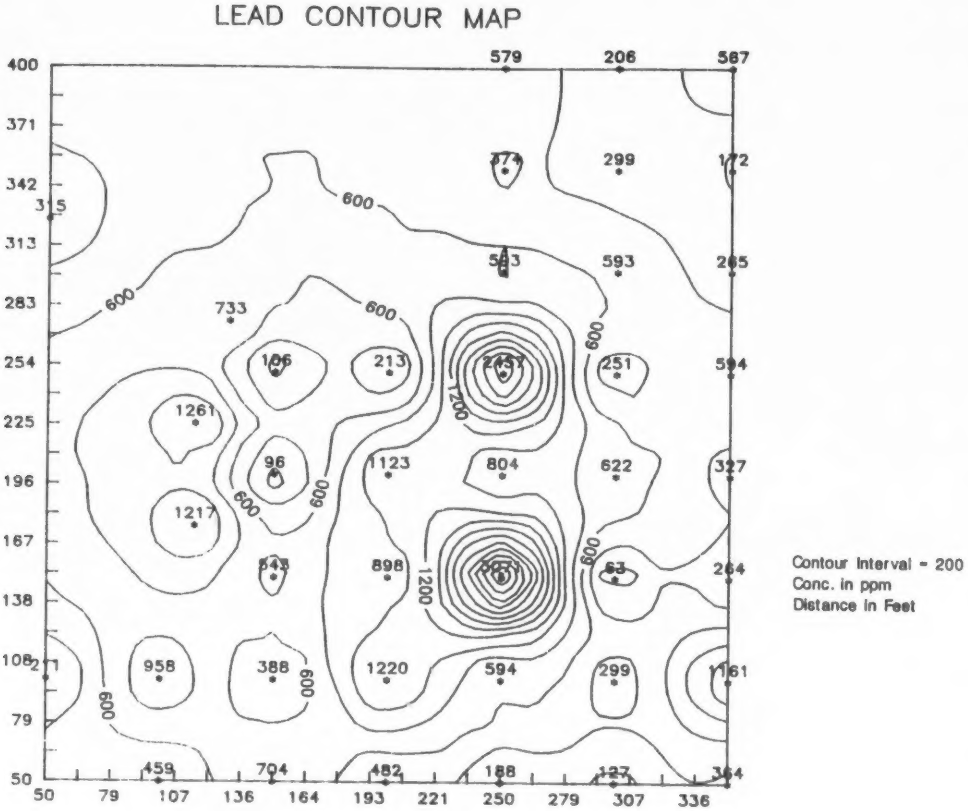

LEAD CONTOUR MAP
400
371
342
313
283
254
225
196
167
138
108
79
50
50
79
107
136
164
193
221
250
279
307
336
579
206
587
374
299
172
315
583
593
285
733
106
213
2457
251
594
1261
96
1123
804
622
327
1217
543
898
3071
63
264
211
958
388
1220
594
299
1161
459
704
482
188
127
364
600
1200
Contour Interval = 200
Conc. in ppm
Distance in Feet

Figure 10

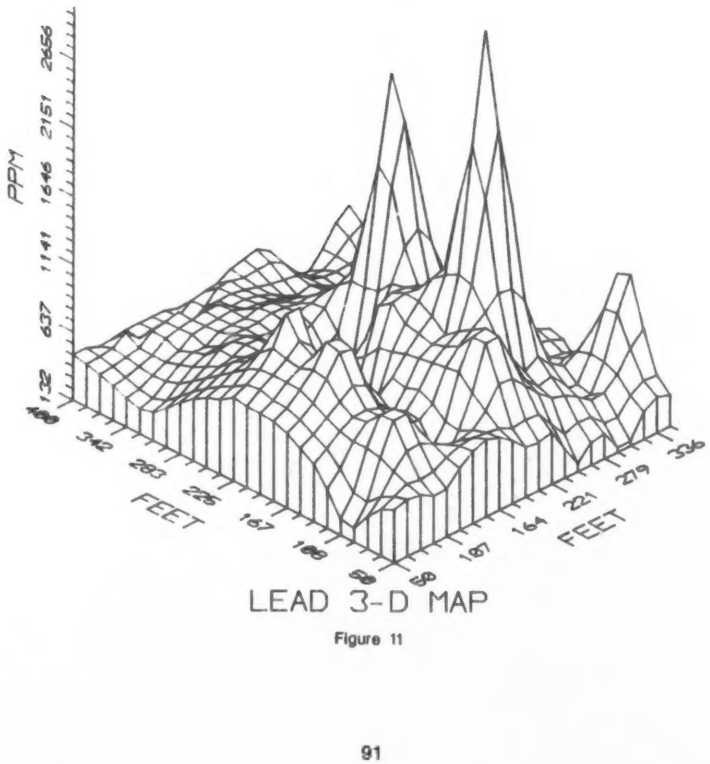
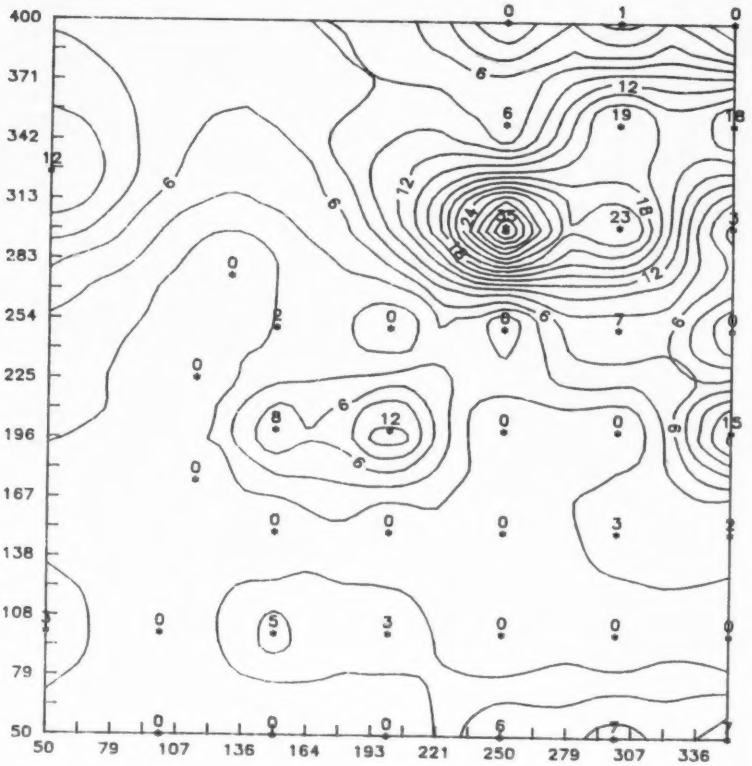


Figure 11

ARSENIC CONTOUR MAP


400
371
342
313
283
254
225
196
167
138
108
79
50
50
79
107
136
164
193
221
250
279
307
336
0
1
0
6
12
6
19
18
12
6
6
12
24
35
23
18
12
12
0
2
0
8
6
7
6
0
0
8
6
12
6
0
0
9
15
0
0
0
0
0
3
2
0
5
3
0
0
0
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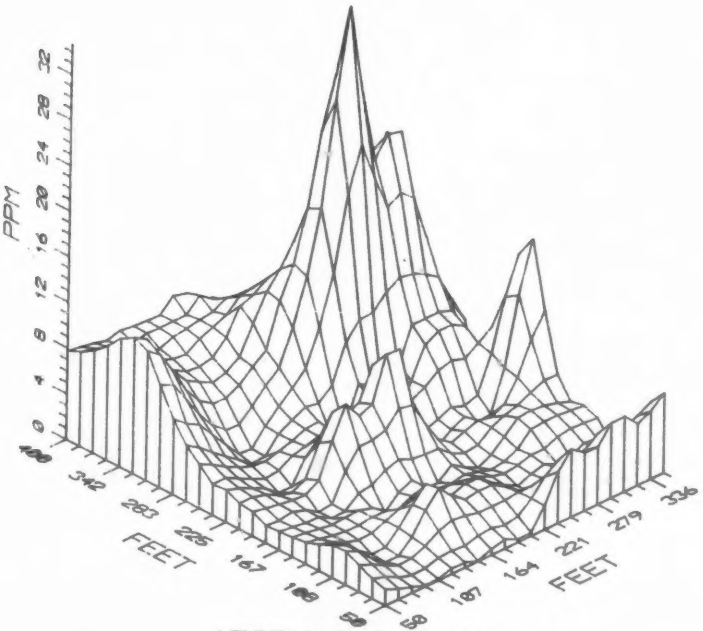
0
0
6
7
7

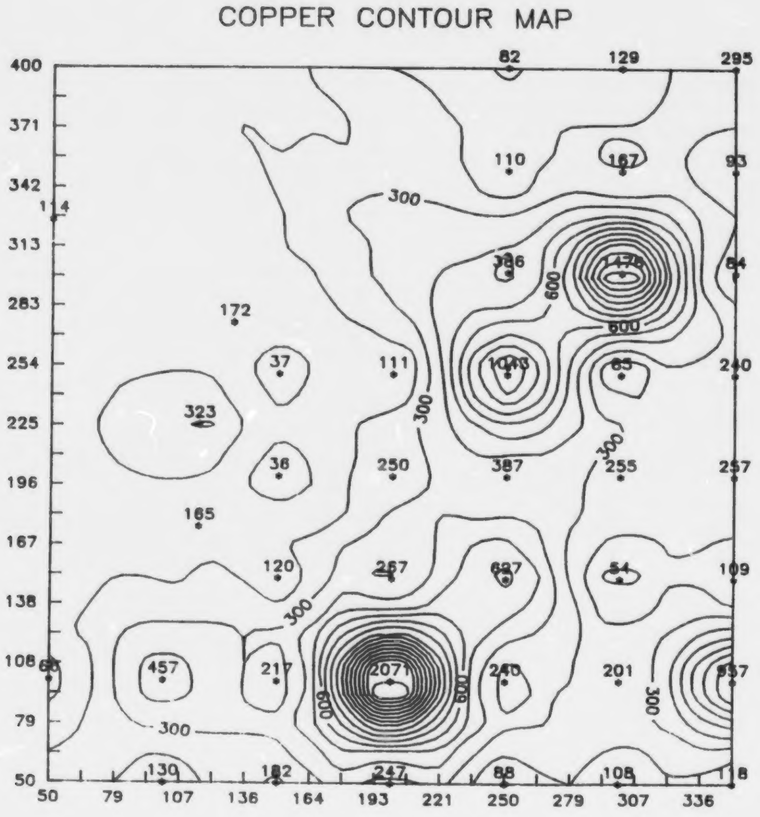
Contour Interval = 2
Conc. in ppm
Distance in Feet

Figure 12



ARSENIC 3-D MAP

Figure 13


COPPER CONTOUR MAP
400
371
342
313
283
254
225
196
167
138
108
79
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79
107
136
164
193
221
250
279
307
336
82
129
295
110
167
93
114
300
386
1476
84
600
172
600
37
111
1040
65
240
323
300
300
36
250
387
255
257
165
120
257
627
54
109
300
457
217
2071
240
201
537
60
600
600
300
300
130
182
247
88
108
118

Contour Interval = 100
Conc. in ppm
Distance in Feet

Figure 14

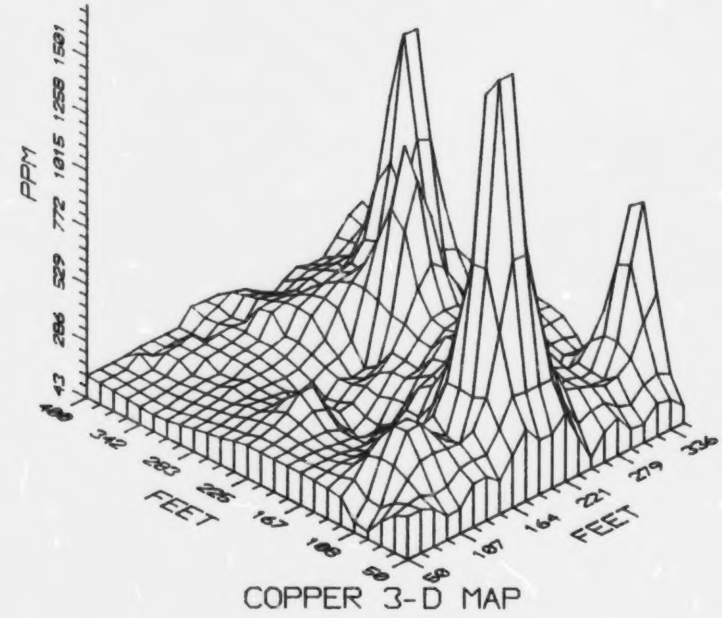

Figure 15

DISCUSSION

HARRY McCARTY: You mentioned the sample disposal problem, and the lack of homogenization, but you also said earlier that you were able to use other tests on the sample, since it's a nondestructive method.

How do your sample sizes compare to what the CLP would use, and do you avoid the problem of having to take splits? You could do XRF, and then send the sample to an analytical laboratory for all the techniques, get two sets of answers on the same sample, and give the lab the sample disposal problem.

RANDY PERLIS: Yes, you could do that, but when we laid out the grid system, there were about 40 samples, and of those, we sent about eight to 10 to the CLP.

This site had already been investigated, as have a lot of sites we do. When we have some idea, we'll still send off the hottest samples that we get to the CLP and try to avoid the sample disposal problem that way.

HARRY McCARTY: Are the sample sizes approximately the same? Would you need the same material?

RANDY PERLIS: No, I believe we collect an eight- or four-ounce jar for the CLP, and we collect about 1.5 mL.

HARRY McCARTY: CLP certainly doesn't use eight ounces for a metals analysis?

RANDY PERLIS: No, but that's what they request.

HARRY McCARTY: Could you conceivably use the same sample size?

RANDY PERLIS: Yes, you could use it out of the same vial. You may run into some sample custody problems that way, if you run it to lab first. Basically, we have co-located samples. We'll take the eight-ounce jar and fill it up, and from that one, we'll homogenize it and mix it up, take a split out of that for us, and then send it on to the CLP.

HAROLD VINCENT: Concerning preparation for a very small sample, did you pulverize before mixing? Did you affect the sample size?

RANDY PERLIS: Yes, we mixed it with a hand mixer, with a mortar and pestle and then sieve.

HAROLD VINCENT: Did you consider briqueting, for both standards and unknowns?

RANDY PERLIS: No, we haven't yet. We were thinking about some other techniques, such as fluxing, but we're trying to keep the sample prep as minimal as possible.

HAROLD VINCENT: I was thinking of briqueting in terms of stability, and you could always relate the standards back to a powder. You could even mix briquets with powders, I would think.

WAVELENGTH TUNABLE PORTABLE LASER

FOR REMOTE FLUORESCENCE ANALYSIS

Gregory D. Gillispie and Randy St. Germain
Department of Chemistry
North Dakota State University
Fargo, ND 58105

ABSTRACT

Direct fluorescence is a sensitive technique for in situ detection of many groundwater contaminants. Details of a compact, high performance tunable dye laser system suitable for such remote measurements are reported. The second harmonic (532 nm) or third harmonic (355 nm) of a pulsed Nd:YAG laser pumps an oscillator plus one or two amplifier stages. The dye laser output is then frequency doubled to generate tunable ultraviolet radiation. The current version of the instrument provides pulse energies of up to 10 mJ in the 560-600 nm region and 300 μJ between 280 and 288 nm with the laser operated at 10 Hz. Better optic sets and optimization of the design should eventually yield at least a factor of three improvement in the pulse energies. With the current version, naphthalene and fluoranthene in aqueous solution have been detected at the ppb level using a simple fiber optic probe.

KEY WORDS: Fluorescence, laser, fiber optic, remote, in situ, analysis

INTRODUCTION

The advantages of fluorescence as an analytical technique are well established. For example, detection limits of about one part per trillion (pg/mL) and below for aqueous solutions of polycyclic aromatic hydrocarbons have been demonstrated in the laboratory setting (1). In addition, fluorescence is a direct method which eliminates the tedious and slow steps of sample concentration, separation, etc. Thus, the response of a fluorescence based instrument to an analyte is virtually instantaneous.

The combination of speed, sensitivity, and specificity makes fluorescence a good candidate for field screening analysis. Moreover, as an optical technique fluorescence can be combined with fiber optic methodology for remote analysis. Chudyk, Kenny, and coworkers at Tufts University were among the first to explore this possibility (2,3). Although incoherent light sources can be used to launch light into an optical fiber for remote fluorescence analysis, the properties of a laser obviously make it the method of choice.

For maximum versatility and ability to distinguish one species from another, the laser light source should be tunable (wavelength selectable). In this work we explore the performance capabilities of a YAG-pumped dye laser suitable for remote fluorescence analysis with fiber optic probing.

EXPERIMENTAL

The apparatus is schematically shown in Figure 1. Key elements of the dye laser are discussed more or less in the order they appear in the optical train.

A. Pump Laser - The Nd:YAG pump source is a Quanta-Ray model DCR-11 operated at 10 Hz. In the Q-switched mode, pulse energies of up to 150 mJ at 532 nm and 60 mJ at 355 nm are available for dye laser pumping. In the work so far, we have only used the 532 nm output to pump Rhodamine 590 and have had to keep the pump power low to avoid damaging the currently available optics.

B. Energy Splitting to Oscillator and Amplifier Cells - A microscope slide beam splitter (BS1) splits off about 8% of the initial 532 nm beam to pump the dye laser oscillator. BS2 is nominally a half-silvered mirror acting as a 50% partial reflector but even at modest YAG pump powers the surface of the partial reflector degrades rapidly, thereby reducing both its reflectivity and transmission. The optimal reflection/transmission ratio of BS2 will be determined by future experiments with high quality dielectric beamsplitters. A likely starting point would be 20% reflectivity of BS2 to pump amplifier cell AC1 with the remaining 80% going to pump the final amplifier cell AC2.

C. Focussing Optics to Oscillator and Amplifier Cells - The doughnut-shaped beam profile of the DCR-11 is somewhat inconvenient for dye laser pumping. However, the combination of a spherical lens and a meniscus lens satisfactorily flattens the beam along its vertical axis and expands it along the horizontal axis sufficiently to focus it to a line image just inside the front face of the flowing dye amplifier and oscillator cells.

D. Oscillator Cell, Amplifier Cell(s), and Circulator - The oscillator and amplifier cell bodies are machined from stainless steel with front and side fused silica windows epoxied to the body. The same dye solution is used for both the oscillator and first amplifier so only a single circulator suffices for both cells. We have found that an inexpensive epoxy-clad magnetic drive centrifugal pump (Cole Parmer model J-7105-00) with flow rate of up to 3 gpm works well. Connections between the pump and the cells are made with polyethylene tubing and Swagelok stainless steel fittings.

E. Dye Laser - The dye laser oscillator is of grazing incidence design (4) and employs a 2400 grooves/mm holographic strip grating (PTR Optics) and an aluminum tuning mirror. The dye laser is operated in the so-called closed configuration where the wedge prism feedback element (Melles Griot, 3°52' angle) is also the output coupler. The tuning mirror is affixed to a precision rotation stage with motorized encoder drive (Oriel model 13028) controlled from a personal computer.

F. Doubling Crystal - An angle tuned KDP crystal in a gimbal mount is used to frequency double the dye laser output. A red corex filter (of the type commonly found on old Beckmann DU spectrophotometers) removes the fundamental but transmits the tunable ultraviolet with good efficiency.

RESULTS

Pumping the oscillator with ca. 3 mJ and the amplifier cell with 15 mJ of 532 nm radiation at 10 Hz repetition rate yielded tunable dye laser pulse energies of about 3 mJ above the Amplified Spontaneous Emission (ASE) level at the peak of the Rhodamine 590 gain profile. The ASE could undoubtedly be reduced appreciably by optimization of the dye concentration, splitting of pump energy between oscillator and amplifier, and variation of the delay time for the pump energy reaching the amplifier cell. However, the presence of high ASE levels is much less of a problem when the dye laser fundamental is to be frequency doubled in a subsequent step. Since as much as 150 mJ/pulse of 532 nm radiation is available from the pump laser, addition of a second amplifier cell and optimization of the operating parameters (and the incorporation of higher quality optics) ought to yield very powerful laser pulses for the generation of tunable ultraviolet radiation.

The collimated dye laser output from the amplifier cell was passed into the doubling crystal without any further focussing. Conversion efficiencies on the order of 5% (on an energy basis) were observed. The frequency doubled output can be separated from the unconverted fundamental with a dispersive prism or with a glass filter.

Our goal is to develop a robust and relatively inexpensive dye laser suitable for field studies. Little work has been done on actual analyses at this stage. However, we did build a simple 2 meter probe of the type described by Scwab and McCreery (5). The 200 um Ensign-Bickford fiber is not controlled for UV transmission and we only included six collection fibers. Undoubtedly, the efficiency of the probe could be greatly improved. Nevertheless, we were able to detect both naphthalene and fluoranthene at the ppb level, even with dispersing the emission in a 0.3 m focal length monochromator.

DISCUSSION

The purpose of the work reported here was more to explore what excitation capabilities are available with a dye laser based system of fairly simple design than it was to show its superiority over a fixed frequency excitation system. Only very preliminary results are available to assess detection limits, but these are very promising.

The ability to tune the laser wavelength is important both for sensitivity and for being able to distinguish different compounds simultaneously present in the sample. The only possible fixed frequency contender for direct fluorescence methods on polycyclic aromatic hydrocarbons is the 266 nm fourth harmonic of Nd:YAG. For benzene, toluene, xylenes, and some of the other one ring aromatics, 266 nm lies quite close to an absorbance maximum and little gain in sensitivity would result from tuning capability. However, for other benzene derivatives such as aniline, p-cresol, or 1,4-dimethoxybenzene, 266 nm lies in a valley of the absorbance spectrum such that a sensitivity loss by a factor of up to ten results from not being able to match the excitation to the absorbance spectrum.

Probably the greater deficiency of fixed frequency excitation is that it severely reduces the hope of speciation, i.e., being able to resolve different species in the sample. Some speciation would be possible by time resolving the emission, thereby exploiting the different fluorescence lifetimes, but the ability to select the excitation wavelength is unquestionably more valuable.

The greatest drawback of the tunable laser system is that more than one dye is necessary to cover the region of interest. If we limit attention to polycyclic aromatic hydrocarbons and their common derivatives, then the spectral region of greatest relevance is between 250 and 300 nm; almost every aromatic compound has one or more strong absorbance bands in this region. At a minimum, two dyes would be necessary to cover this region. Moreover, with 532 nm pumping the shortest achievable dye laser wavelength is about 550 nm, which gives a short wavelength limit of 275 nm after frequency doubling. This is inadequate to reach many mono-ring systems (e.g., benzene, toluene, xylenes). To achieve fundamental coverage in the λ < 550 nm region requires pumping of another dye, say coumarin 500, with the 355 nm Nd:YAG output.

Although changing dyes in the field is possible, it is a tedious processs and would severely limit how many samples could be measured in a given time. A better alternative is to have separate oscillator cell/amplifier cell/circulator combinations for each one of the dyes to be used so the dyes can be rapidly changed, although any wavelength selective optics would also have to be changed when the pumping wavelength is changed between 532 and 355 nm. Even more flexibility would be achieved if a separate dye laser were built for each dye. Clearly this is only feasible if the dye laser itself is very economical. With commercial dye lasers costing $20,000 and up, it would be out of the question. The design we have followed makes multiple dye lasers feasible. A instrument with two dye lasers, one for pumping Rhodamine 590 with 532 nm and one for pumping Coumarin 500 dye with 355 nm YAG output would give coverage of the desired 250-300 nm region after the frequency doubling.

CONCLUSION

We have built a relatively simple dye laser which provides significant power levels of tunable ultraviolet radiation when pumped with a Nd:YAG laser. The laser system is amenable to incorporation into a field instrument and efforts along these lines are underway. We believe that detection limits of 1 ppb or better are feasible for polycyclic aromatic hydrocarbons in groundwater.

ACKNOWLEDGMENT

This work was supported by a cooperative agreement between North Dakota State University and the United States Geological Survey, which provided the Nd:YAG pump laser. Financial support from the North Dakota Water Resources Research Institute is also gratefully acknowledged.

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RS: ROTATION STAGE
G/TM: GRATING/TUNING MIRROR
BS: BEAMSPLITTER
CL: CYLINDRICAL LENS
ML: MENISCUS LENS
OC: OSCILLATOR CELL
WP: WEDGE PRISM
AC: AMPLIFIER CELL
M: MIRROR
DC: DOUBLING CRYSTAL

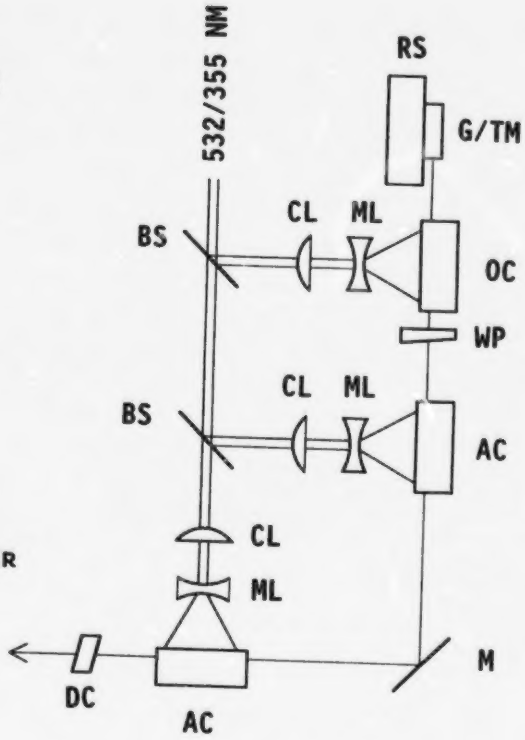
532/355 NM
RS
G/TM
BS
CL
ML
OC
WP
BS
CL
ML
AC
CL
ML
M
DC
AC

FIGURE 1 - LAYOUT OF DYE LASER

FIELD SCREENING FOR AROMATIC ORGANICS USING LASER-INDUCED FLUORESCENCE AND FIBER OPTICS

Wayne Chudyk, Kenneth Pohlig,
Nicola Rico, and Gregory Johnson

Civil Engineering Department
Tufts University
Medford, MA 02155

ABSTRACT

The prototype field instrument developed by our research team uses remote laser-induced fluorescence (RLIF) to measure aromatic organics in-situ. Using a laser as light source, and fiber optics to carry light to the bottom of a well and back up again, a method for direct measurement of fluorescent ground water contaminants has been shown to be a useful field screening method. Field results using sensor lengths up to twenty meters are presented.

A typical measurement proceeds as follows. A fouling-resistant sensor made of fused silica glass, PTFE, and stainless steel, of length corresponding to well depth, is placed in the water in a well. Sensors are inexpensive enough to be dedicated to wells for long-term monitoring applications. After well purging, fluorescence measurements are taken and compared to previously characterized standards. Results are expressed as total aromatics concentration in ppb or ppm. Usual sampling time, including setup and decontamination, is on the order of fifteen minutes per well.

Results to date indicate good correlation between GC (Method 602) and RLIF; rapid response time; and good sensitivity, with ppb-ppm results routine. Analyses to date include primarily BTEX (from gasoline), and aromatic solvents (phenol, cresols). Due to the short analysis time, independence from outside laboratories, and comparable instrument capital cost, RLIF is shown to be a cost-effective alternative to GC for routine screening of aromatics. Where a large number of wells need to be examined over a short time, and aromatic organics are the suspected contaminants of interest, the advantages of RLIF become even greater.

Conclusions show that the prototype field screening tests have been successful, indicating the feasibility of the RLIF method. It is shown to be applicable to sites where aromatic organics are known or suspected problem compounds. Since aromatic organics include the benzene, toluene, and xylenes fraction of gasoline, as well as over half of the organics on the EPA Priority Pollutants List, RLIF is applicable to a variety of hazardous waste sites. It should be useful for monitoring and characterizing fuel spills (BTEX), coal tar sites (phenols and cresols), and aromatic solvent sites.

INTRODUCTION

In-situ field screening methods have become attractive because they eliminate sample handling and resulting changes in sample composition. Analysis is also performed in real time, avoiding decision delays resulting from the usual wait for laboratory reports. Our method uses fluorescence spectroscopy to measure aromatic organic compounds in-situ. Fiber optics have been suggested as useful tools for ground water monitoring, since they can allow measurements to be made at distance from the material of interest (1, 2, 3). By using fiber optics and a laser as the light source, measurements can be performed at distances of practical application to monitoring wells.

Prior Work in RLIF Development and Use

Fluorescence analysis has proven to be an attractive method for screening aromatic components in water. For example, fluorescence has been previously used in the laboratory to identify and quantitate contamination of water by petroleum products (4), as well as in studies of the petrographic composition of the organic matrix in soils and rocks (5). The RLIF application is in using a similar approach with a portable field unit.

The present configuration of the field prototype forces it to be less sensitive than laboratory instruments, so that RLIF is currently best used as a screening tool. As advances in instrument technology develop, we hope to expand the limits of our method. Extensive testing has proven the usefulness of RLIF in simulated well setups, and limited field testing was performed with the first RLIF field-portable prototype (6, 7, 8). The second-generation prototype was constructed in modules that could be easily temporarily mounted in a minivan or four-wheel-drive vehicle for field testing. Reduction in size of the RLIF instrument has allowed easier access to field sites with a smaller vehicle. Further field testing on existing contaminated sites, in parallel with GC analysis, has answered questions concerning the effectiveness of RLIF in measuring such contamination. The results of this study demonstrate its short analysis time and potential for screening large numbers of wells versus laboratory GC analysis.

FIELD SCREENING WITH RLIF

Field sampling using the second RLIF prototype has progressed successfully. In the first two quarters of 1988, sites sampled included twelve gas stations, two manufacturing companies, and one chemical company. Site geological characteristics varied from fractured bedrock through glacial till to sandy silt. Weather conditions ranged from wind chill factors of -21°C (-5°F) through freezing rain to balmy 25°C (77°F) afternoons. Contaminant characteristics varied, while most data concern gasoline and petroleum product spills or leaks. For example, a typical gas station site contained at least five wells at varying depths. In field measurements, a series of sensors ranging in length from five to thirty meters was used. Field decontamination of the sensors used detergent, methanol, and distilled water. Field repair of sensors was also shown to be practical.

Samples obtained from the same wells at the same time as our tests were analyzed by an independent laboratory (Groundwater Technology, Inc., Norwood, MA).

RESULTS

RLIF response was calibrated using serial dilutions of gasoline in the laboratory. To eliminate effects of signal attenuation versus sensor length, calibration was performed using sensors of the same length as used in the field. Figure 1 illustrates such a calibration curve for gasoline ranging from tens of ppb to hundreds of ppm using a ten meter sensor. A least-squares curve fit was used to match the field RLIF response to the calibration curve, yielding a corresponding concentration. The laboratory results from the same field sites were tabulated and the total concentration of aromatics detected, corresponding to what RLIF should detect, was calculated. For each data set, this total aromatics concentration was compared with RLIF response for the same well. Figure 2 shows RLIF response versus gas chromatographic (GC) response for samples from six of the sites, with RLIF response usually higher than GC values.

CONCLUSIONS

Field determinations of aromatic ground water contaminants, such as the BTEX fraction of gasoline, have been shown to be successful using RLIF. Good correlations exist between RLIF results and EPA Method 602 GC determinations. As a rule, such correspondence between the methods shows that RLIF is a useful screening method,since its response is in real time. It is clear that savings in time and convenience of RLIF over GC make RLIF attractive as a field screening method.

ACKNOWLEDGEMENTS

The assistance of Groundwater Technology, Inc., and Goldberg-Zoino and Associates for providing access to field sites and data is deeply appreciated. The authors are thankful for the support of the National Science Foundation, the USEPA through the Tufts Center for Environmental Management, the USGS, and the Alexander Host Foundation.

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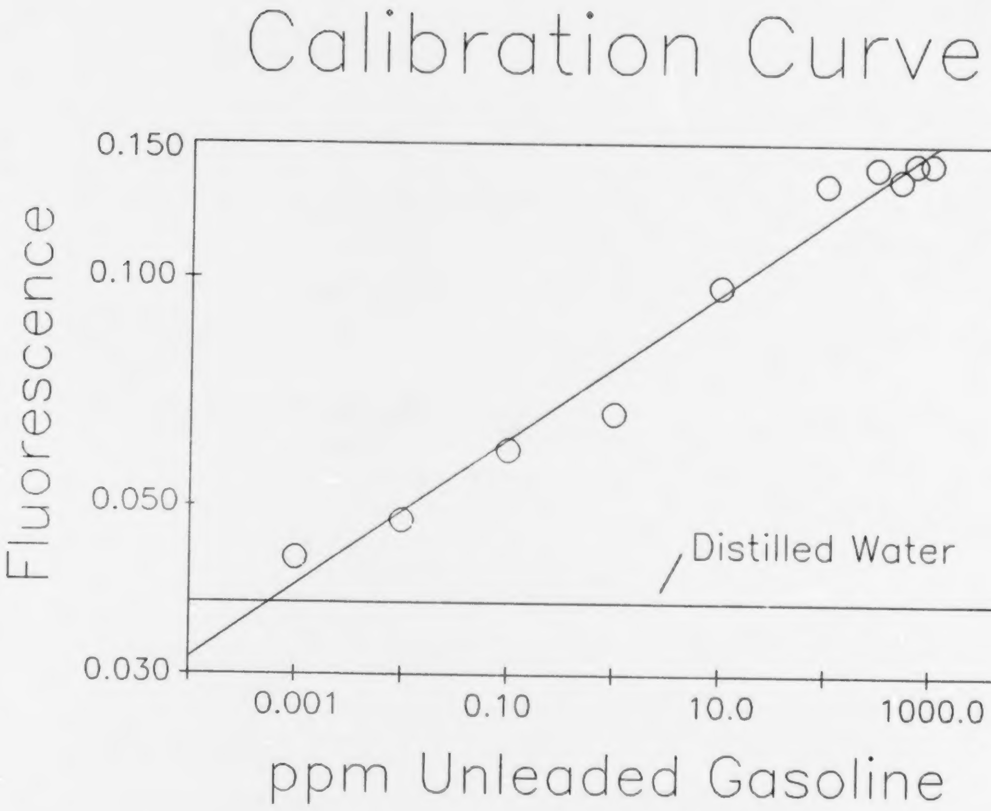

Figure 1. RLIF Calibration Curve for Unleaded Gasoline Using a Ten Meter Sensor

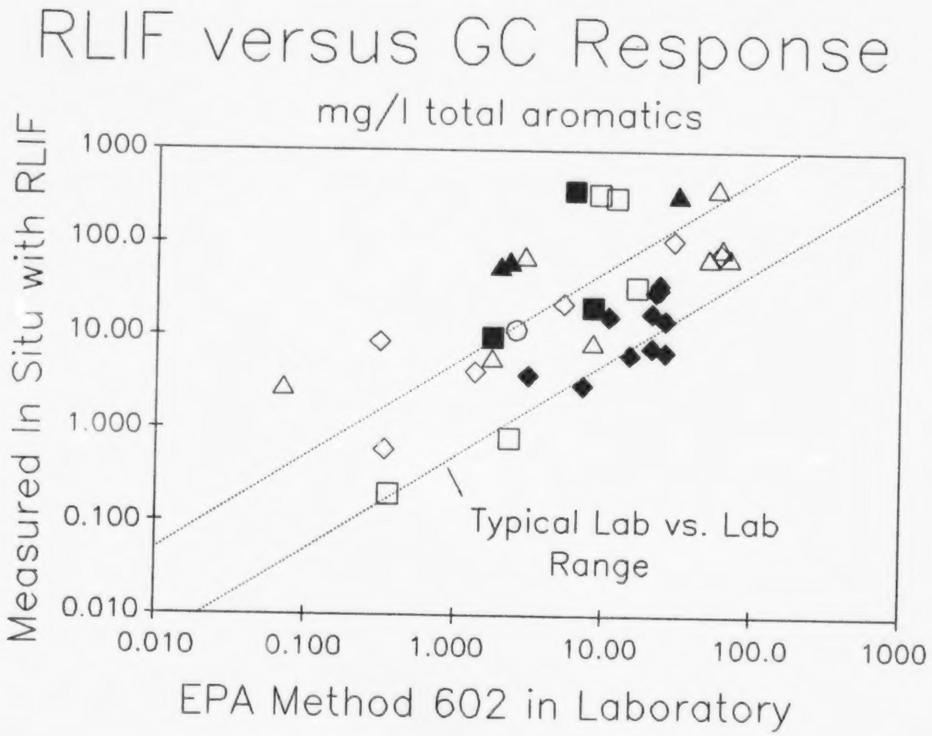

Figure 2. RLIF Response Versus EPA Method 602 for Total Aromatics

DISCUSSION

JOE ANDRADE: Could you elaborate on the optical design of the sensor itself? Your abstract you says that the sensor is designed to be fouling resistant. Could you elaborate on that?

WAYNE CHUDYK: We used two fibers – one excitation and one collection fiber. They are positioned in the sensor head so that they overlap – they would have overlapping exit cones if you were to issue light out of both of them. The excitation cone overlaps the collection cone from the emission fiber. This is covered by a patent, so I don't want to go into too much detail.

The fouling resistance relates to the materials which include stainless steel, silica glass, or Teflon. At some of the gasoline sites, we have a lot of iron bacteria, that tend to grow on everything. We have not seen them interfere with our sensors, even though they have been left in the ground for a period of up to five weeks. We have more work to do in that area, so I didn't report the data.

The idea, though, is to have something that is not amenable to supporting biological activity, and we feel we have succeeded.

DELYLE EASTWOOD: The bar diagram you showed gave the fluorescence of a number of species, some of which were mixtures. Mixtured fluorescence will vary with where it's excited.

Secondly, you don't make a clear distinction between GC and GC/MS. I believe you were actually talking about method 624, which is a GC/MS method, and you should have indicated that.

Finally, you don't make a clear difference between humic and fulvic. The fulvic is actually the soluble component. I have done work with humic and fulvic acids, and they can fluoresce over a wider range, depending on what the source is. They will fluoresce a little bit almost any place you excite them.

Do you intend to look at other fluorescing species besides gasolines and in complex mixtures? Are you looking at UV fibers, in terms of being able to see fluorescence under 300 nanometers?

WAYNE CHUDYK: The fibers that we have now are ultraviolet transmitting fibers. We tend to cut off around 300 nanometers, because we have scatter from the laser excitation (at 266). We also pick up a water Raman line around 293, 295. Those things interfere with what we're able to see. In general, we look from 300 to 500 nanometers.

Regarding looking at other components, we are experimenting with different filter combinations and also different monochromator types of approaches. The biggest problem with have seen with monochromators relates to field reliability. A monochromator in the back of a van, doesn't work after a while.

We have not been successful in taking monochromators out. So that has restricted our use to the glass cut off filters.

JOHN KOUTSANDREAS: Could you address the problem of not being able to drive that station wagon into place? How portable is the equipment?

If the sensors are left in place over a period of six months, what kind of degradation do you have?

And finally, what kind of eventual cost do you see for commercialization of this unit?

WAYNE CHUDYK: In terms of portability, we have the system in modules, each weighing a maximum of 40-50 pounds. There are two of them that are that big, and two of them are much smaller.

We usually operate out of the back of the van, because of weather conditions in New England. However, we have successfully carried the modules a few hundred yards into a place that is not van accessible.

In terms of making the instrument smaller, the instrument that we have now can be carried in pieces, and can operate any place you can get a generator. The next prototype we expect to be even smaller, and even more portable. All of the components that we have now in the prototype are designed to operate off 12 volts, and that's a step we expect to take in the future as well. So we'll free ourselves from a generator.

The second question was the lifetime of the sensors. We have only been able to leave sensors in the ground for a few weeks at a time. We would like to leave them in the ground much longer. We don't expect problems, with the exception of a couple of wells with very heavy bacterial growth. Those monitoring wells had inert casings, and the iron bacteria were even sliming up those. Our sensors were not in the ground long enough for us to accurately evaluate that.

I would expect in a "normal" situation, where you did not have that heavy type of growth, that these sensors should stay relatively clean, and usable.

One of the things built into the system is the ability to measure power, both before the laser light goes down and after it comes back. So we have the ability to check the integrity of a sensor, even a sensor that's been left in place. The first thing that's done on a site with a sensor that's been left in place is to check if the power is going down by approximating what the power should be.

We have that ability to see if the sensor is okay. Did somebody pull it out and snap a fiber, and shove the thing back in the ground, or is there something funny happening to the end? We can check that relatively rapidly.

The instruments cost approximately $30,000 to construct, one at a time. The single most important piece is the laser, which costs around $12,000 in single quantities. They tell us there would be quantity discounts, but we haven't approached lots of 100 or whatever. I would expect the final cost to drop to the twenties, if not lower, if this were to be commercialized.

GREG GILLISPE: When you were illustrating the dynamic range for gasoline, changing concentration over a couple orders of magnitude, you were only getting a change in signal of two, three, five, or something like that. Can you explain why you're not getting an order of magnitude change in signal for an order of magnitude change in concentration?

WAYNE CHUDYK: The way the signal is massaged after it comes out of the PMT's, in terms of the conversion from current to voltage, gives us a number that we could save. We could integrate over longer periods, and that will give us a larger number.

GREG GILLISPE: What I am referring to is that an analytical criterion for a method is that the signal be linear in concentration, and yours seems to deviate very substantially from that. Whereas in the Richardson-Andall paper, for example, their linearity went well down to the parts per trillion. So I am troubled by the deviation.

WAYNE CHUDYK: So are we.

MIKE CARRABBA: You presented a slide that showed the GC/MS data versus your data, and it is a little troublesome that there were some places where there were maybe two or three orders of magnitude difference between your data and the GC/MS. I'm quite confused by that. I could see an order of magnitude, but three orders of magnitude is quite a large difference. Can you explain?

WAYNE CHUDYK: Frankly, in some cases, we resampled and found errors. There are, as you well know, many cases where things can slip between the field and the lab.

The differences that concern us the most are where the numbers that we see don't match the numbers that they see, and are off by at least an order of magnitude.

I am not sure if that is a potential interference. In other words, are we seeing something that they are not seeing, which is the most likely case, or is there something that we're overlooking? We're still trying to figure some of that out. That's the nature of research.

SECOND-DERIVATIVE ULTRAVIOLET ABOSRPTION
MONITORING OF AROMATIC CONTAMINANTS IN GROUNDWATERS

J. W. Haas, III   E. Y. Lee
C. L. Thomas   R. B. Gammage
Health and Safety Research Division
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831-6113

ABSTRACT

A portable spectrometer for second-derivative ultraviolet absorption spectrometry (DUVAS) has been evaluated for the screening of aromatic contaminants in groundwaters. Benzene, its derivatives, and polycyclic aromatic hydrocarbons were found to be amenable to analysis by this technique at concentrations down to 1 ug/mL. Based on these encouraging results, construction of a rugged, underwater fiber optic probe for direct, down-well pollutant monitoring using DUVAS has begun. A prototype of the probe was used successfully to obtain spectra in the laboratory. When the new probe is completed it will be used to monitor benzene in a groundwater well at a hazardous waste site.

INTRODUCTION

Surface and subsurface water contamination is a growing problem in the U. S. which can be attributed primarily to the indiscriminate dumping of hazardous chemicals into the environment. The severity and widespread nature of this problem require that polluted waters and their sources be located rapidly and cost-effectively. Gas chromatography with mass spectrometric detection has been a useful tool for identifying polluted sites and the hazardous chemicals in them. This method is costly, however, and other less expensive, yet reliable, analytical techniques should be considered when many samples are to be tested for contamination.

Second-derivative ultraviolet absorption spectroscopy (DUVAS) is a well-established analytical technique with distinct advantages for screening water samples. Complete spectral analysis takes about one minute and a single wavelength can be monitored every few seconds in an instrumental "dwell" mode. No sample preparation is required prior to analysis; even turbid samples can be analyzed directly. These features, coupled with the relatively low expense of a spectrometer, render DUVAS a cost-effective screening tool. The method is particularly well-suited for identifying some of the most common pollutants, aromatic hydrocarbons (including benzene, its derivatives, and polycyclic aromatic hydrocarbons), at levels as low as 1 ug/mL. Furthermore, the portability of the DUVAS instrument allows for on-site screening and monitoring of migrating pollutants.

The scope of recent research has been to determine which priority pollutants are amenable to analysis by DUVAS and to develop a new version of the instrument for field analysis. Incorporation of fiber optics into the new spectrometer was undertaken to allow for direct analysis of subsurface well waters.

POLLUTANTS AMENABLE TO DUVAS ANALYSIS

A review of the literature indicated that benzene, toluene, ethylbenzene, xylenes, chlorobenzenes, phenol, and naphthalene have been the aromatic contaminants detected in groundwater most frequently. Therefore, our DUVAS spectral library, which was comprised primarily of polycyclic aromatic hydrocarbons found in synthetic fuels, was expanded to include these compounds. Spectra were collected from 200-350 nm for the pollutants. Each spectrum was unique, allowing individual compounds to be identified in the presence of the other species tested. Even the three xylene isomers were easily differentiated using DUVAS. A minimum detectable concentration was also determined for each pollutant using its predominant spectral peak (Table I). The results were similar for all species, being about 1 ug/mL.

Table I

Minimum Detectable Concentrations
of Common Aromatic Pollutants

compound	nm*	ug/mL+
benzene	254	2.4
toluene	268	1.9
ethylbenzene	268	2.0
o-xylene	270	3.8
m-xylene	272	1.9
p-xylene	274	1.0
chlorobenzene	271	4.5
o-dichlorobenzene	277	3.3
phenol	277	2.2
naphthalene	311	0.5

* Wavelength of the determination
+ Minimum detectable concentration (S/N = 2)

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Linear dynamic ranges for the compounds studied were also nearly uniform, spanning over a 100-fold concentration range.

The ability to detect benzene and toluene has a useful application in monitoring fuel spills, a frequent groundwater contamination problem. Both benzene and toluene are major components of gasolines and other fuels and can thus be used as markers for these pollutants. Figure 1 shows benzene and toluene spectra, and a spectrum for a water sample contaminated with JP-4 jet fuel. Benzene and toluene were easily identified without interference from other species in the sample. Their presence was confirmed by gas chromatographic analysis (photoionization detection) which also showed that these two compounds were the predominant aromatic hydrocarbons in both the water sample and the jet fuel.

A shallow groundwater well at the base of a hill into which organic waste was once poured has also been monitored with DUVAS. The spectrum (Figure 2) was dominated by benzene which was quantitated at 30 ug/mL. Gas chromatographic analysis with FID detection confirmed the presence of benzene at a comparable level (40 ug/mL). The higher value obtained with the gas chromatographic method may have resulted from interfering compounds in the sample. The chromatogram was complex, with numerous overlapping peaks from chlorinated solvents and other aliphatic hydrocarbons present at comparable levels in the sample. These species offered no interference to the DUVAS analysis.

FIBER OPTIC DUVAS

A disadvantage of most methods used to screen groundwaters for pollutants is the need to collect samples and transport them to the laboratory. Contamination and degradation of samples are important concerns which our portable spectrometer reduced by allowing DUVAS analyses to be made in the field. However, samples still had to be drawn from wells, which maintained the possibility for contamination, required fully attended operation of the instrument, and precluded continuous well monitoring. The solution to these difficulties was considered to be the development of a down-well, fiber optic probe for the spectrometer. Two probe configurations were considered as likely candidates for down-well monitoring and they are shown in Figure 3. In the first probe configuration, light from a monochromator (MONO) passes to a transmission probe through one fiber and returns through a second fiber to a detector (D) located in the spectrometer. In the second design, the detector (a small, solid state device) is integrated into the probe and the electrical signal is carried back to the spectrometer for processing (ELECT). The latter configuration was considered because of the poor transmission of ultraviolet light through optical fibers; it gave twice the working distance of the first design.

A laboratory prototype of the fiber optic probe was constructed according to the second configuration. A light-tight box represented the probe housing and contained a silicon photodiode detector, a sample cuvette holder, and a lens. The lens focused light emerging from the end of the fiber, through the cuvette to the detector. The other end of the fiber (600 um, plastic clad hydroxylated silica) was coupled through two lenses (collimating and focusing) to the output of the monochromator. A 150 W xenon lamp was used as the source of ultraviolet light.

Figure 4 is a spectrum of 25 ug/mL phenol obtained with the prototype instrument equipped with a 5 m optical fiber. The spectrum was the same as one collected with the spectrometer prior to its modification. Calibration curves were also determined for phenol using 1, 5, and 44 m fibers. As shown in Figure 5, the 1 and 5 m fibers gave curves which varied little from the one obtained without an optical fiber. Ultraviolet light transmission was attenuated greatly in the 44 m fiber, however, resulting in a calibration curve with a much smaller slope. Despite the limitations for quantitative analysis posed by the small slope, phenol was still detected down to about the same minimum detectable concentration with the long fiber as was attained using the shorter fibers.

CONCLUSIONS

The results for phenol demonstrated that down-well contaminant monitoring using DUVAS with a fiber optic probe was feasible. Spectra obtained for other aromatic pollutants using the prototype probe were also comparable to standard spectra in our library. On the basis of these results, construction of a rugged underwater probe has begun. The new probe will incorporate an all-silica optical fiber for improved ultraviolet transmission (up to 100 m is expected) and will be tested at the groundwater well containing 30 ug/mL benzene. The well will be monitored over an extended period of time to follow changes in the benzene concentration caused by movement of the polluted plume, microbial degradation, or other factors.

ACKNOWLEDGEMENT

Research sponsored by Division of Facility & Site Decomissioning Projects, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

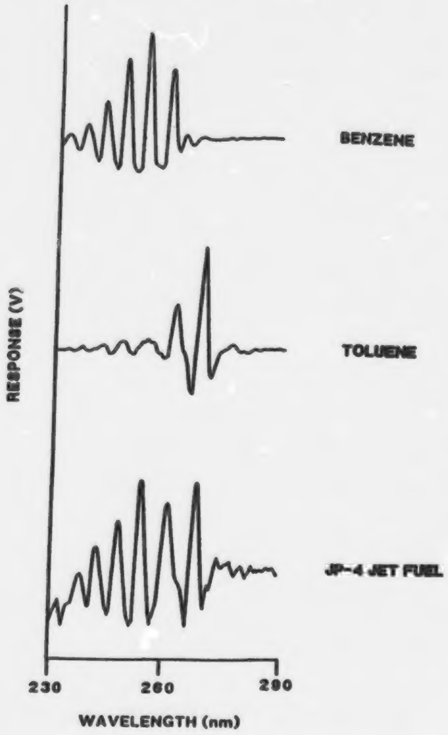

Figure 1 - Benzene and Toluene are Markers of Fuel Contamination

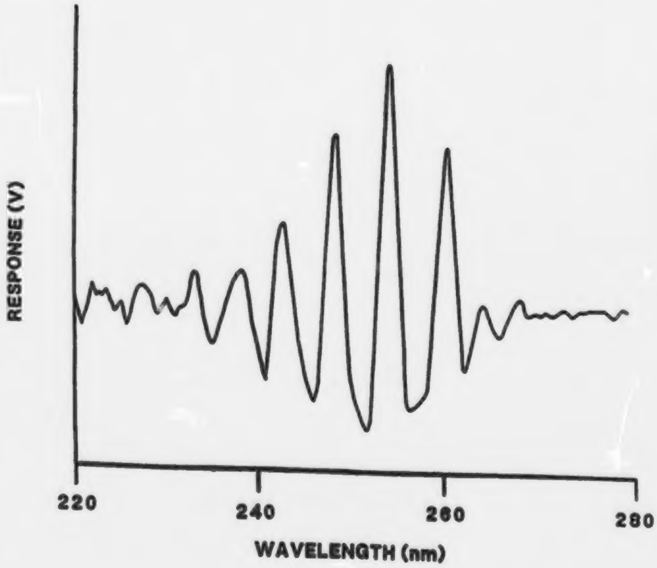

Figure 2 - Groundwater Contaminated with Benzene

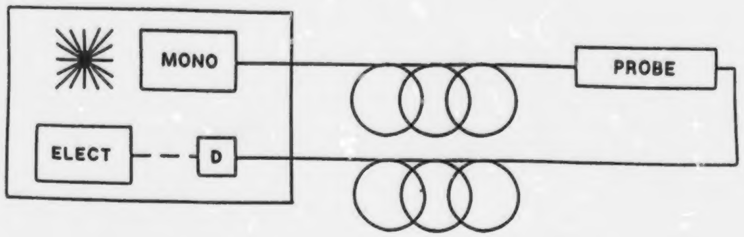
MONO
PROBE
ELECT
D

Figure 3A - Dual Fiber Optrode for DUVAS

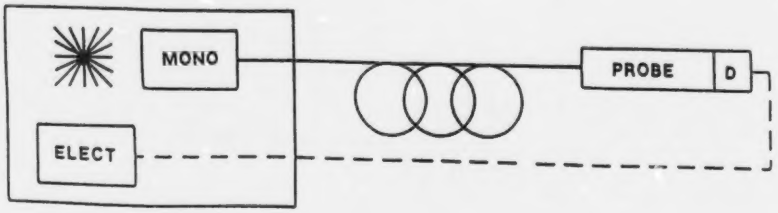
MONO
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Figure 3B - Single Fiber Optrode for DUVAS

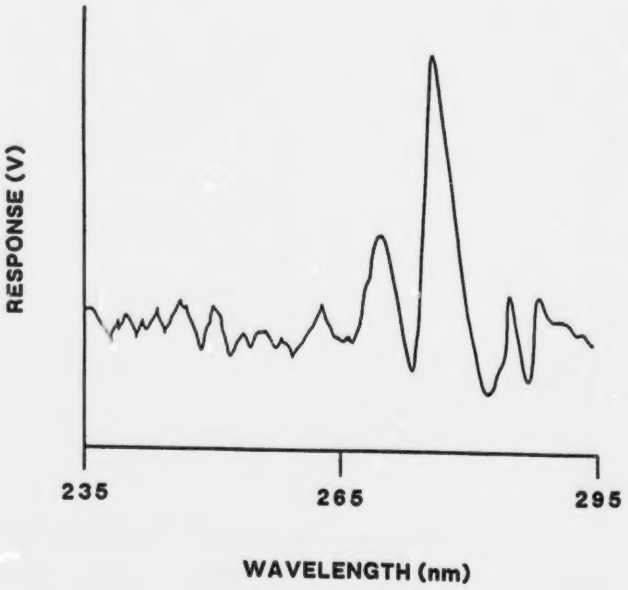

Figure 4 - Phenol Spectrum Using a 5 Meter Fiber

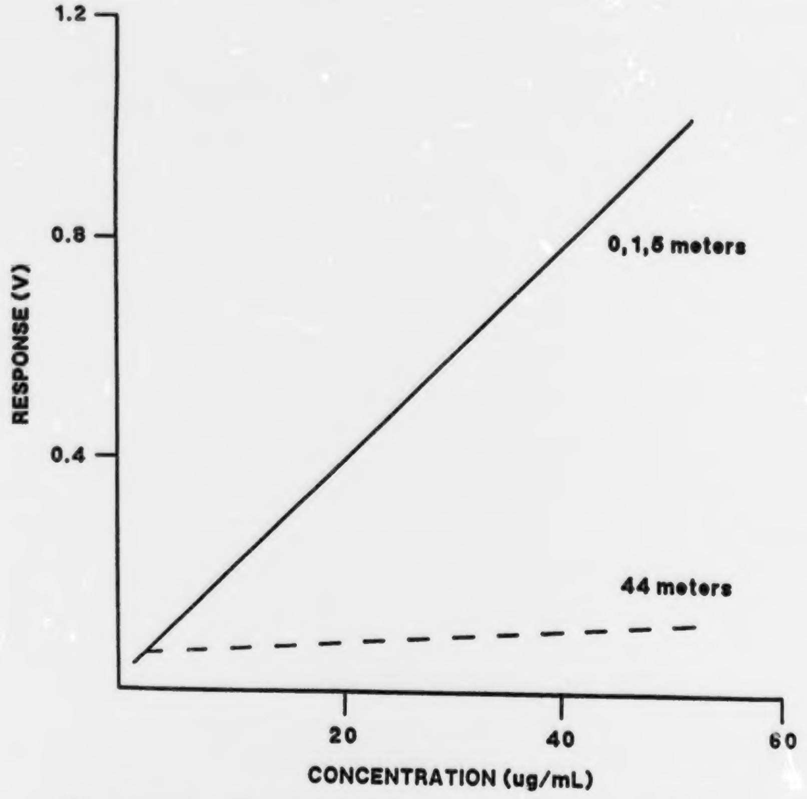

Figure 5 - Phenol Calibration Curves Using Different Lengths of Optical Fiber

DISCUSSION

DELYLE EASTWOOD: Why are you doing this on UV absorption, instead of fluorescence? Fluorescence can also be used in the derivative mode. O'Hagar did it, and Purcell did it, actually separating about 14 pinholes by derivative fluorescence spectroscopy. Fluorescence is at least potentially much more sensitive, and I believe all the compounds that you showed actually do fluoresce.

JOHN HAAS: Benzene doesn't fluoresce very well, but the other ones do better.

DELYLE EASTWOOD: It is a low yield, but it still fluoresces if you use a good control.

JOHN HAAS: There are a couple of advantages to this technique. First, we had the instrument sitting in the laboratory, and second, we were asked to monitor this well for benzene. It's ideally suited for that. Also, the insensitivity to turbidity in the sample will allow us to go in to muddy situations particularly at this plant. This might be much more of a problem with fluorescence.

JOHN SCALERA: Do you have any problems with critical angle on your UV construction, your fiber optic leads? In other words, do you keep them fairly straight and parallel in all your designs, and monitoring?

JOHN HAAS: We tried curling the fibers around the room with the 44 meter one. So long as it's fixed on the two ends, going into the detacher, and also coupling to the output of the monochromator, we didn't see any difference in the spectra. The end going into the detector isn't so crucial, because we use a pretty large size. It's one centimeter across, so we can focus down, and we have a little bit to spare there.

JOHN SCALERA: You didn't lose any intensity with the bending, using the ultraviolet frequencies?

JOHN HAAS: You could see minor shifts, but when you take the derivative, essentially, that washed out. So long as we can have 100 to 200 milliwatts of intensity of light going through, then the derivative still ends up looking the same.

MAHMOUD SHAHRIARI: Do you see the potential for using a UV absorption technique in an evanescence mode, instead of the direct-gap technique that you just mentioned?

JOHN HAAS: It's possible, but I think the porous approach is better, because the intensity of the light getting out through the evanescence is not as great. We don't have to worry about losses out the end of the fiber, or from coupling. We are using it more as a light medium, so we get the full intensity that we can possibly get through the fiber, and with UV, that's a major consideration.

MAHMOUD SHAHRIARI: Can you comment on what type of fibers are you using for transmitting UV?

JOHN HAAS: We have actually used plastic clad fiber so far, and we look for much better results when we go to the all silica fibers. Also, I will test some liquid core fibers. But right now, we were very pleased to get anything through these fibers, from what we had reported. These are 600 micron cores from general fiber.

HAZARDOUS WASTE ANALYSIS BY RAMAN SPECTROSCOPY

Charles K. Mann and Thomas J. Vickers
Department of Chemistry, Florida State University
Tallahassee FL 32306-3006

ABSTRACT

The application of ultraviolet resonance enhanced Raman spectroscopy to chemical analysis of low concentrations of organics in complex samples is described. The physical observation consists of illuminating a sample by a beam of ultraviolet radiation and analyzing the light that is scattered by the sample. The phenomenon is applicable to solids, liquids, and gases; however in this work, analyses are limited to samples in the liquid state. Two modes of operation are discussed. In one, the analysis is applied to the effluent from a high performance liquid chromatograph (HPLC). The sample is fractionated completely or in part by the chromatograph. Individual components are identified and quantitated by means of the spectroscopic signal. In the second mode, the analysis is carried out by direct Raman measurement upon the sample. Discrimination of target substances from the bulk is accomplished by using resonance enhancement which allows the response of specific classes of compounds to be enhanced as compared with the bulk of the sample.

To achieve limits of detection which can be used in trace analysis, it is necessary to perform the measurements with ultraviolet (UV) exciting radiation. At this time, lasers which produce adequate power in the UV operate in the pulsed mode. Although average power is not especially high, the energy is delivered in short bursts, producing a high photon flux which can bleach the sample. To avoid this, it is necessary to provide an unconventional coupling between the radiation and the sample. The apparatus is discussed. The fact that absorption peaks in the UV are not necessarily wide as compared with Raman shifts leands in some cases to a situation in which the use of an internal standard does not adequately correct for the effect of sample absorbance on exciting radiation power. The cause of this effect is discussed and the necessary corrective steps are outlined.

INTRODUCTION

The methods which currently are most used for determination of organic compounds in hazardous wastes, gas chromatography (GC), HPLC, mass psectroscopy (MS), gas chromatography-mass spectroscopy in combination (GC/MS), and GC/FTIR, each offer certain advantages and are constrained by certain limitations. GC/FTIR and GC/MS offer very good selectivity and, especially for GC/MS, excellent sensitivity. They are contrained by the necessity to have the sample in the vapor state during the separation. HPLC provides excellent separating power and is applicable to nonvolatile and thermally labile compounds. However, the detectors which are used with it do not provide a very satisfactory combination of sensitivity with generality of application.

Raman spectroscopy also offers certain advantages and is limited by certain constraints. In the context of hazardous waste management, some of the advantages offered by Raman measurements permit the handling of samples which cause problems with other methods. The basic physical principles upon which it is based are firmly established. Raman scattering has been applied to chemical analysis in solid and liquid samples. It is particularly applicable to samples that are dissolved or slurried in water. The actual measurement is carried out by directing a beam of radiation onto the surface of the sample. Measurement is made by capturing and analyzing that radiation which is scattered from either the surface or the interior of the sample. The technique is applicable to nearly all of the substances on the E.P.A. Priority Pollutants List, including nonvolatiles.

Analytical uses of Raman are based upon the high information content of its

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signals. Raman signals are one form of molecular vibrational spectra, IR spectra are another. It has been recognized for decades that vibrational spectra are characteristic properties of molecular structures, very much as finger prints are characteristic of humans. It is this very high degree of specificity in type of signal produced which serves as the basis for applications to chemical analysis of mixtures. Raman differs from IR in two important aspects. It is well suited to application to condensed phase samples and it can provide high enough sensitivity through resonance enhancement to be useful in trace analysis.

Raman measurements can be made directly on solids without regard for the sample thickness. IR measurements on solids, whether idspersed in a transparent matrix or directly by diffuse reflectance, do not produce the high accuracy and reproducibility which is required in order to do mixture analyses. Raman measurements are well suited to accurate measurements on liquid samples. Although chemists have traditionally used IR for liquid samples, attempts to achieve high accuracy fail because of the impact of refractive index changes on shapes and intensities of absorbance bands. Whether the measurement is made in a cell fitted with two windows or with one having only one fixed boundary, an attenuated total reflectance cell (ATR), the details of the shapes of peaks are appreciably affected by refractive index changes. (1,2) These effects are large enough to interfere with attempts to make use of subtle differences in band position and shape in mixture analyses. This is important because it is necessary to have linear performance in order to do generalized mixture analyses. Accordingly, Raman measurements are appropriate to the analysis of effluents from high performance liquid chromatography (HPLC) columns and to direct determination of organic compounds in natural samples.

The fundamental sensitivity of resonance enhanced Raman spectroscopy has been demonstrated (3-7) to be sufficiently high to support analyses at the part per billion level without the necessity for concentration. Resonance enhancement is an effect that occurs when the wavelength of the incoming radiation corresponds to an absorption band of a component in the sample. The signal produced by that component can be enhanced, by as much as a million-fold, compared with its unenhanced signal. This provides a powerful method for discriminating the enhanced compound from other sample concomitants which are not enhanced. The limits of detection of unenhanced Raman measurements are comparable to thoseof IR measurements, usually between 0.05 and 0.10 percent.

If it is desired to carry out a sample preparation step, such as extraction of animal tissue, the extract would ordinarily furnish a suitable sample. Successful application to complex samples depends upon the ability to elicit very intense and very characteristic responses of narrowly targeted compounds, or classes of compounds, in the presence of much larger concentrations of sample concomitants. This is a very special capability of Raman spectroscopy which occurs when resonance enhancement is used.

Most compounds which cause concern owing to pollution problems are colorless, absorbing only in the ultraviolet. Accordingly, it is necessary to use UV radiation. At this time UV laser radiation is available either from visible sources from which UV radiation is obtained by frequency doubling or tripling, or from light generated in the UV by an excimer laser. We have been using an injection-locked excimer laser as a source.

HPLC APPLICATIONS

The technology of HPLC is of course very well developed. This research is concerned with coupling the chromatographic column to bring the optical signal to the spectrometer and with data treatment required to analyze the results. In principle, a Raman spectrometer is coupled to a chromatograph by directing the light beam onto a transparent exit section of the column. In doing this, allowance must be made for the high photon flux produced by pulsed lasers, the need to minimize detector dead volume, and for the necessity to achieve high efficiency in collecting the scattered radiation. These questions must be considered together in the design of an HPLC detector cell.

HPLC Cell Design

In order to achieve adequate average power to give useful sensitivities, the laser must be operated at high pulse energies. The resulting photon flux density may be sifficient to bleach solutions which contain absorbing samples. This does not usually involve any permanent chemical change in the system, simply a depletion of the concentration of the ground state species which causes nonlinearities in the relationship between concentration and signal intensity. It does not cause nonlinearities that affect peak shapes. Two measures are being taken to control sample exposure. First, the laser intensity is monitored and the output of the monitoring transducer is used to control a beam attenuator which determines the photon flux at the sample.

The second measure involves coupling the laser beam to the chromatographic effluent in a way that avoids focusing the beam sharply in order to reduce the photon flux density. Several factors must be considered. Performance of an HPLC detector is critically affected by its dead volume. Light coupling must therefore be arranged to produce a minimum increase. There are two related factors which must be considered. Conventional spectroscopic optics do not efficiently collect light produced from a diffuse source. When light is collected and taken to the spectrometer, the optical constraints encountered in taking it into the instrument are quite severe.

Accordingly, simply defocusing the beam to reduce photon flux density gives unsatisfactory results owing to reduced collection efficiency. We reduce flux density by introducing the light beam to the solution through a bundle of silica optical fibers. Available fibers are approximately 100 micrometers in diameter. Accordingly, a large number can be used without drastic increase in the size of the chromatographic outlet tube. Thus, instead of focusing the entire beam at a point in the sample, the beam power is first attenuated according to the number of fibers used. Each of these is brought individually to the sample, achieving the desired reduction in local intensity. This arrangement permits efficient collection of the scattered radiation, since the scatter produced by light emitted by each fiber can be taken back through the same fiber. This gives fl/ collection efficiency. At the spectrometer, the beam must be imaged on the entrance slit in order to make it fall on the grating where it can be used. This is accomplished by designing the fiber bundle to match the slit cross section.

The use of fiber optic coupling introduces two additional signal components: the Raman signals produced by silica and the effects of solarization. The Raman spectrum of silica can be determined very accurately and corrected for by the usual methods that are used for removal of interferences, e.g., by including it as one of the references in a least squares fit.

Solarization is a gradual degradation of the optical properties of silica which is exposed to UV radiation which ultimately makes it necessary to replace the fibers. An internal standard corrects for the effect in quantitative measurements. When light is introduced into a sample for a Raman measurement, the effective intensity is affected by sample absorption of both the incoming and scattered radiation. Experimental variations are compensated in emission spectroscopy by using an internal standard. However, in resonance enhanced operation, not all effects of absorbance by either the analyte or sample concomitants are always compensated. An internal standard is entirely effective if the sample absorbance is the same for the radiation scattered by both the analyte and the internal standard. The situation is illustrated in Figure 1. Experimental error is plotted against absorbance at the analyte wavelength for values of analyte/standard absorbance, X. When the ratio is unity, there is no error. Positive or negative error occurs when the ratio deviates from unity.

A general purpose instrument operating in the ultraviolet must be expected to encounter this situation because the absorption bands which occur are fairly sharp. It is therefore necessary to provide a compensating mechanism other than the conventional internal standard. Two factors are important: the solution absorbances at the wavelengths scattered by the analyte and internal standard and the transfer function of the sample collection optics. We have demonstrated earlier (8) that the sample absorbance can be calculated from examination of the variation in intensity of scattered light. Basically this is a matter of alternating measurements with the laser and with a continuum source and can be done under computer control by swinging a mirror into the laser beam to block it and admit light from the other source. The transfer function of the fiber optic collection system is set by the entrance cone to the fiber, which is known, and the sample absorbance, which is being determined. Accordingly all necessary variables are known.

DATA PROCESSING

If the chromatograph effects a complete fractionation of components in the sample, identification and quantitation of them by Raman spectroscopy is straight forward. A reference spectrum is needed and the instrument must have been calibrated. If fractionation is incomplete, data processing often can be treated as a problem in multicomponent analysis. (9) The effluent from a chromatograph constitutes a favorable medium for multicomponent analysis and Raman measurements are especially well suited to this application.

When fractionation is incomplete and when the information that is required to treat the problem in terms of multicomponent analysis is unavailable, it is sometimes possible to extract additional information by means of factor analysis and related chemometric techniques. Starting with the pioneering work of Lawton and Sylvestre (10), a considerable effory has been made in this direction. (11-13) For those situations in which no information about the analyte is available, unequivocal results are obtained only for two component mixtures. However, when some information is available, it is possible to include it in the basis for the calculations. The partial least squares technique, which has been described in detail by Haaland (14), can be applied to this type of problem. This will involve furnishing calibration sets which form the basis of the calculation.

DIRECT ANALYSIS

The background now exists to perform a range of analyses on complex samples without the necessity for prior separations. This basically involves making use of spectroscopic and data processing steps to cause the signals of specific target compounds to be discernible against the background produced by all other components in the system. Its success depends upon producing sensitive signals from the target compounds and in devising methods for discriminating them from other signals. The benefits from this operation are ability to perform the analysis without altering the sample and very rapid turn-around time.

At this stage we use samples in a liquid form, either as solutions, extracts, or as slurries of solid samples in a suitable solvent. We assume that analyses are targeted at specific compounds for which reference spectra are available. It is assumed that, for a given class of analysis, typical samples would be available upon which to base an analytical design. These do not have to constitute a training set, just some typical examples. This design would primarily involve selection of conditions which would be incorporated into custom software which would in turn control the actual analysis. Analyses would be targeted at components in the range of parts per million to parts per billion. Higher concentrations could be handled by dilution.

The design of a sampling device for direct analysis is quite similar to design of an HPLC detector that is described above. The major difference is that for direct analysis, it is not usually necessary to be greatly concerned about the volume of the detector.

In contrast to the application in chromatography, direct analysis depends upon the spectroscopic detector for analytical selectivity. The bulk of a sample such as plant or animal tissue, soil or ground water consists of materials which do not absorb light and will therefore not show enhancement. The signals produced by these sample constituents consist of a large number of individual components which combine to produce a largely featureless background on which the resonance enhanced signals are detected as discrete peaks. A successful analysis depends upon achieving a sufficient degree of enhancement to make the peaks stand out. It also depends upon being able to distinguish target compound signals from those of interfering compounds which happen also to show enhancement. In general distinct functional groups produce spectra which are different enought to be measured separately. If a target substance contains the same functional group as a background component, they will be detected together.

Operating in the direct analysis mode, a determination takes from one to five minutes, including time for data processing. The actual process is largely done under computer control, with the most critical judgments taken by the person responsible for configuring the soft ware.

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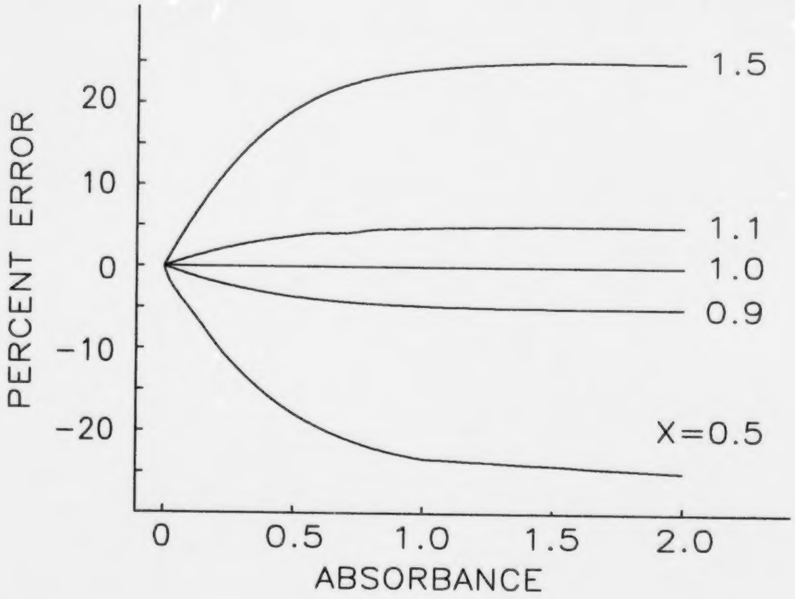

Figure 1. Effect Of Analyte/Internal Standard Absorbance Ratio, X

DISCUSSION

GREG GILLISPE: How much power would you need in the UV to implement the tunability? How much would you want for it to be a viable alternative to your Raman shifter?

CHARLES MANN: I think what you were describing earlier was adequate. That's why during the course of the morning, I have altered my view of what may be necessary to do resonance-enhanced Raman. I was prepared when I came here today to say that we will have to use an eximer laser, and a Raman shifter, but after listening to what you had to say, I'm not quite so sure of that now.

It seems to me that we might very well be thinking about the possibility of using a dye laser if what you say about it being easy to change from one dye to another, and its compactness is true. The diode-tunable YAG laser is a reality that sounds like a very interesting possibility.

GREG GILLISPE: When you do have tunability, how much of an increase in the resonance enhancement can that give you?

CHARLES MANN: Very big. The best results are if the excitation is right on the top of the resonance bin, and then tapers off quite rapidly. There are some other aspects of this that are very interesting. If you have real tunability, then you can begin to use the different spectra produced as a result of doing your analysis twice – once at one wave length, and once at another.

Tunability will allow you to discriminate not only against those compounds which do not resonance enhance, but will also give us another handle on an attempt to get interferences out of these mixtures that the environmentalists keep asking us to analyze.

NELSON HERRON: I just encountered small portable nitrogen lasers, with dye cells that are about $5,000. You just pull the cubette out, and they have a battery pack for them. I think Laser Science is the name of the company. You may know of it and want to comment on it.

GREG GILLISPE: It's a nice toy. It's a very nice laser, and you can get tunability with it, but the power levels are pathetically inadequate for these purposes. I believe the nitrogen pump laser, at 337, is in the vicinity of a few hundred microjolts. The dye laser gives you 20 microjolts when you double frequency. Perhaps you can double, but your power levels just become abysmaily small. I don't think it can be applied in this sort of study.

JONATHAN KENNY: You can double those lasers, and get three nanosecond shots. So it's really a very low powered device.

About your Raman shifter, you said you got 15 angstrom intervals. What kind of fill gas were you using?

CHARLES MANN: I was using hydrogen, and deuterium, and methane.

JONATHAN KENNY: A mixture of all three?

CHARLES MANN: No, I don't think so. I was under the impression we were going to have three of these pipes that we would put into the machine. As far as I can see from looking at them, they are just pipes, and there is nothing especially critical about that.

JOE ANDRADE: In our experience with the pulse laser systems and biological compounds, the photo bleaching proves to be a horrible problem. Is there any advantage to going beyond microjoules, or even antijoules per pulse, if you're going to have photo bleaching problems? Why can't you simply use low power pulses and integrate through a bunch of pulses to get a signal level.

CHARLES MANN: There isn't any point in going to larger pulses. But we think, from the point of view of quantitative analysis, there is a real point in going to parallel pulses. By using an optical fiber bundle, we could put easily 100 fibers in the bundle and take the light from each pulse 100 times to the sample. That will reduce the flux density, obviously, by a factor of 100. It will not completely eliminate the bleaching, but will increase the dynamic range by roughly a factor of 100.

PROTOTYPE DESIGN AND TESTING OF TWO FIBER-OPTIC SPECTROCHEMICAL EMISSION SENSORS

Khris B. Olsen Jeffrey W. Griffin
Danny A. Nelson Bradley S. Matson
Pacific Northwest Laboratory
P. O. Box 999, K6-81
Richland, Washington 99352

Peter A. Eschbach
Department of Physics
Washington State University
Pullman, Washington 99164

ABSTRACT

A unique radio frequency-induced helium plasma (RFIHP) sensor and a spark discharge (SD) sensor were designed, and prototype units were developed and tested. Both sensors use an atomic excitation source coupled to a fiber-optic cable and optical spectrometer to monitor in situ the emission intensity of selected elements of interest in the ambient air. Potential applications include vadose zone monitoring of volatile species. The RFIHP and SD sensors were designed to measure in situ concentrations of chlorine-containing compounds. The results of this research demonstrate proof of concept of the theory, but suggest further refinements are necessary to achieve detection sensitivities sufficiently low to be useful for monitoring concentrations of selected elements in vadose zone air.

Key words: Helium plasma, spark discharge, spectrochemical sensors, fiber-optic sensor, in situ monitoring.

INTRODUCTION

Since 1986, staff at the Pacific Northwest Laboratory (PNL) have been developing and evaluating new chemical sensor concepts suitable for real-time, multipoint environmental monitoring. The chief impetus for this research has been the need to better understand transport mechanisms of contaminants in the subsurface environment at the Hanford Site in southeastern Washington State. For these measurement scenarios, fiber-optic sensors have many attractive features, such as a small probe size, a multiplex advantage (i.e., multiple probes with one central detection and data acquisition system), and the potential for fast response. In addition, these sensors have other potential applications as monitors and alarms for a variety of processes relating to other industrial and government operations.

There is specific interest in developing sensors capable of real-time, in situ monitoring to detect selected elements in groundwater and chlorinated hydrocarbon vapors in vadose zone wells at Hanford. During past operations at Hanford large quantities of process-related inorganic and organic chemicals used in the production of special nuclear materials were released to the environment. For example, several hundred tons of carbon tetrachloride have been disposed to the ground during past operations at the Plutonium Finishing Plant.(1) Recent groundwater monitoring efforts have detected carbon tetrachloride in monitoring wells at concentrations exceeding 1000 times the drinking water limit. Furthermore, carbon tetrachloride has been measured in the outgas from vadose zone wells at concentrations exceeding 200 ppmv. Preliminary data collected around the Hanford Site indicate that carbon tetrachloride is migrating both in the groundwater in the aquifer and as a vapor through the vadose zone. Currently, the areal distribution of the carbon tetrachloride is reasonably well defined in Hanford groundwater; however, the extent of areal carbon tetrachloride contamination in the vadose zone is unknown. Before serious consideration can be given to remediation technologies, rapid, cost-effective techniques must be developed to accurately identify major vadose zone accumulations of carbon tetrachloride and other contaminants present in the subsurface environment at Hanford.

Two fiber-optic sensors based on optical emission techniques using a radio frequency-induced helium plasma (RFIHP) source and a low-voltage spark discharge (SD) source are currently under development at PNL. These two technologies were selected because they interface well with fiber-optic technology and have the potential of measuring in situ concentrations of selected metals and nonmetals in vadose zone air and groundwater.

Atomic emission sources based on noble gas plasmas interfaced to gas chromatographs (GC) and optical spectrometers have been extremely useful to the analytical chemistry community as element-specific detectors since proof of concept was first demonstrated by McCormack et al. in 1965.(2) Since then, most of the work cited in the literature on specific-element detectors focused on the microwave-induced helium plasma (MIP) as the preferred excitation source for GC detection.(3,4,5) The GC-MIP system provided sufficiently low detection limits and elemental specificity for most elements of interest. However, a major drawback of the MIP source was the plasma's inability to remain stable or, in some cases, ignite when air was injected into the carrier gas stream. Operating a stable plasma with small but measurable quantities of air without destroying its excitation characteristic is a critical requirement for a detector designed to measure total chlorine in vadose zone air. In 1985, Rice et al. published the results of a study using a low-frequency, high-voltage, electrodeless-discharge plasma (RFIHP).(6) They found that this plasma had detection limits in the picogram range for several elements, including chlorine, phosphorous, sulfur, and mercury. They also found that the plasma was reasonably tolerant of the presence of contaminants and air. Additional advantages included the compactness of the plasma source and its low helium consumption. To take advantage of all the favorable characteristics of the RFIHP, PNL has designed an element-specific prototype sensor capable of measuring carbon tetrachloride in air.

Electrical sparks have long been used as an excitation source for spectrochemical analysis.(7) Consideration of electrical spark excitation for the SD probe was inspired by recent work by Cremers et al. (7) describing the use of laser-induced breakdown spectroscopy (LIBS) for the analysis of liquid samples.(8) The electrical spark offers unique advantages for real-time environmental sensing. First, the spark simultaneously provides sample vaporization, molecular dissociation, and elemental excitation. This makes the excitation mechanism suitable for vapors, solid aerosols, and most importantly, liquids. Second, the electrical spark is essentially a generator of atomic emission lines; that is, molecular species are generally entirely dissociated (at some time during the spark lifetime or immediately afterwards), and emission spectra are observed for atoms and ions. Third, sparks are relatively easy to generate, and they are well suited for remote environmental probes. Disadvantages of the spark excitation method include a high level of variability in optical emission from spark to spark (up to 50% in our measurements), severe Stark broadening of spectral lines, which effectively lowers wavelength resolution in the emission spectra, and the generation of an intense continuum emmission. However, the potential to supply additional information related to in situ concentration of selected parameters associated with the migration of contaminants significantly outweighs any of the known drawbacks.

EXPERIMENT

Radio Frequency-Induced Helium Plasma

A schematic diagram of the prototype RFIHP probe and related operating parameters is shown in Figure 1. This design is a variation of the design by Rice et al.(6) Major differences from the published design include 1) the use of a 6-mm-OD x 1.2-mm-ID quartz tube as the plasma chamber, 2) placing a 10-μm-ID, 38-mm-long segment of uncoated capillary column at one end of the plasma tube (used as a critical orifice), 3) operating the plasma chamber at subambient pressure, and 4) viewing the plasma axially. The overall experimental system is shown in Figure 2. Fiber-optic input/output coupling geometries are shown in Figure 3. Because of inherent limitations in fused-silica optical fibers, measurements are only possible over the wavelength range of 400-1000 nm. A conceptual design of a field probe is shown in Figure 4. Nominal plasma cell and electro-optical detection system operating parameters are summarized in Table I. The probe concept was evaluated as a detector for chlorinated hydrocarbons or fluorochlorocarbons via detection of neutral chlorine emissions at 8379.97 Å. Detectability investigations were performed with carbon tetrachloride, 1,1,1 trichloroethane (1,1,1 TCA), and dichlorodifluoromethane.

Spark Discharge

A schematic diagram of the prototype SD probe is depicted in Figure 5. The overall experimental system is shown in Figure 6. The operating instrumental parameters used during this experiment are summarized in Table II. Note that for the laboratory measurements, the trigger signal was provided by monitoring spark emission from the top of the probe. This was necessary because of the long delay between the input to the trigger module and actual spark initiation. This trigger mode also minimized jitter-induced noise resulting from variation between the spark time position and the gate time position in the boxcar averager.

Calibration Apparatus

A Metronic Dynacalibrator Model 340 was used to generate known concentrations of carbon tetrachloride to determine the detection limits of the RFIHP sensor. The permeation chamber on the calibrator was operated at 50°C with a chamber flow of 171 mL/min. A 3.81-cm-long diffusion tube with a cross-sectional area of 0.1963 cm^2 was used to emit known concentrations of carbon tetrachloride into charcoal-purified air. The diffusion tube was filled with 3 mL of Burdick and Jackson "Distilled in Glass"-quality carbon tetrachloride. The diffusion tube was allowed to equilibrate to temperature for 1 h before calibrations began.

RESULTS AND DISCUSSION

Radio Frequency-Induced Helium Plasma Probe

Spectral wavelength scans near the Cl(I) 8375.97 Å line for increasing 1,1,1 TCA analyte are reproduced in Figure 7. This analyte was introduced into the RFIHP by placing a cotton swab soaked with 1,1,1 TCA adjacent to the capillary tube inlet. Apparent in all the scans are the oxygen peak located at 8446.38 Å and the increasing peak intensities at 8428.27 Å and 8375.97 Å caused by neutral chlorine emission from the 1,1,1 TCA. The RFIHP sensor responds to a variety of other chlorinated species including dichlorodifluoromethane (Freon-12) and carbon tetrachloride (Figure 8). This behavior would be anticipated because this detector responds to the chlorine atom contained in the three aforementioned compounds. However, the relative intensity of the chlorine emission for the same concentration of a given component dependents on the percentage of chlorine in the molecule being measured. Thus, the RFIHP sensor would produce a chlorine intensity twice as intense for carbon tetrachloride as for dichlorodifluoromethane.

Because the RFIHP detector is incapable of speciating any of the chlorine-containing compounds, it is imperative to identify the chlorinated hydrocarbon of concern so estimates of contaminant concentration can be made.

A calibration curve of sensor response versus analyte concentration (carbon tetrachloride) in air determined that the prototype probe had a lower detection limit of 500 ppm. It is important to note that several factors affect the intensity of the spectral emissions of chlorine in the helium plasma. These factors include 1) operating pressure, 2) air bleed rate through the capillary column (i.e., sample flow rate) into the plasma, 3) helium flow rate (which determines sample dilution), 4) RF excitation power, and 5) the location of the plasma viewing along the axes of the plasma tube. Little attempt was made to optimize these parameters for the reported demonstration experiments. While the reported detection sensitivities reported by Rice et al. (6) are excellent for high-purity, atmospheric-pressure helium plasma, significant degradation of the plasma excitation properties is expected when the concentration of the air in the helium plasma exceeds 1%. However, the 45-μL/min flow rate of air through the capillary tube into the plasma is significantly less than 1%; therefore, it appears that additional air could be metered into the plasma without significantly degrading its excitation potential. This increased air flow could further decrease detection limits for chlorine.

The primary use of the RFIHP detector on the Hanford Site would be to measure the concentration of carbon tetrachloride in the vadose zone air or for continuous, long-term carbon tetrachloride monitoring in well head space. However, indirectly estimating the concentration of carbon tetrachloride in the groundwater by using the Henry's law constant is another application of the RFIHP detector. This estimate, however, assumes the concentration of carbon tetrachloride in air directly above the water (within a few inches) is in equilibrium with the concentration in the water. In Mack and Shiu (9), the Henry's law constants for carbon tetrachloride estimate a partitioning ratio between air and water at equilibrium to be approximately 0.95 to 1.0. This ratio estimates that for each microgram per liter of carbon tetrachloride in the water the air concentration would be approximately 150 ppbv. Thus, by applying this relationship, the RFIHP sensor could estimate the concentration of carbon tetrachloride in groundwater from concentration values determined from air just above the water/air interface. However, it is uncertain at this point whether perturbations introduced by fiber-optic probes would cause deviations from Henry's law behavior.

Other industrial applications of the RFIHP sensor include monitoring for concentrations of selected species in air, such as mercury, fluorine, or phosphorus. The species could exist in the gas phase or be associated with an aerosol. The monitoring could be related to hazardous vapor detectors and alarms or process control monitoring.

Spark Discharge Probe

Representative spectra from 3000 - 6000 Å for the air spark appear in Figures 9A-C, in which the presence of a strong continuum can be seen throughout the spectral region. In addition, the spectral region between 3000 and 4600 Å contains several peaks, most likely attributed to NH and N_2^+ molecular bands. The region above 4600 Å is considerably less complicated, particularly between 4600 and 4900 Å where numerous Cl(II) atomic lines are located. Figure 10 is a scan of the spectral region between approximately 4600 and 4950 Å without the presence of a chlorine-containing compound (lower trace) and with the presence of carbon tetrachloride (upper trace). The most intense line in the spectra is at 4779.54 Å because of the Cl(II) emission line. Because of the poor detection limit (~100,000 ppm) no attempt was made to produce a calibration curve.

From the results of the initial experiment it is clear that the SD probe can cause molecular dissociation and elemental electronic excitation. However, it clearly is not the detector of choice for measuring the concentration of chlorine-containing compounds in air. The real potential for this probe may be for measuring the concentrations of selected metals in groundwater. The SD probe has more possible applications than the RFIHP probe. It has the potential to be used to excite vapor samples, liquids, or aerosols to determine concentrations of selected elements (metals). However, it cannot be used in a explosive environment because of its excitation mechanism.

CONCLUSIONS

Two concepts for fiber-optic spectrochemical emission probes based on emission spectroscopy have been demonstrated. Further work is required to optimize operating parameters for the RFIHP probe to determine the ultimate lower detection limit for chlorine. The SD probe will be evaluated in aqueous solutions during 1989. The target detection limit for chlorine using the RFIHP probe is 1 ppm, and the detection limit for selected metals using the SD probe will have to be below the drinking water limits of those selected metals (5-50 ppb). Both the RFIHP and the SD probe have great potential for environmental monitoring applications where real-time, in situ measurements are required. The use of fiber-optic spectrochemical emission probes will be an advantage in cases where chemical interferences to other types of sensors [surface acoustic wave (SAW) and fluorescent] are anticipated and where chemical species of concern have no highly specific reaction. Finally, the probes do not use any expendable materials; their lifetimes should greatly exceed that of fiber-optic probes based on colorimetric or fluorimetric chemical reactions. Consequently, they are well suited for continuous environmental monitoring over extended periods of time.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

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Table I. Experimental Operating Parameters for the RFIHP Probe System

Plasma Operations

Pressure: 200 torr
Helium Flow Rate: 50 mL/min
Air Sampling Flow Rate: 45 µL/min
Excitation Frequency: 278 kHz
Excitation Voltage: 9.1 kV p-p
Power: 52 W (load), 70 W (forward)

Electro-Optical System

Chopper: 140 Hz
Blocking Filter: ORIEL RG780
Slit Width: 500 µm
Scanning Rate: 3Å/sec
Lock-In Sensitivity: 10-100 mV
Lock-In Time Constant: 0.08 sec

Table II. Experimental Operating Parameters for the SD Probe System

Box Car Averager

Gate Width: 6 µsec

Sensitivity: 100 mV, 1V, 2V
Input: DC/1MΩ
Averaging: 10 pulses
Rep. Rate: 20 pps

Photomultiplier

Tube: Hamamatsu R1828.01

(WA 1324)84.11
Voltage: 1.2 kVDC

Spectrometer

Slit Width: 20 µ/m

Filter: WG335,
GG475 (ORIEL)
Scan Rate: 1Å/sec

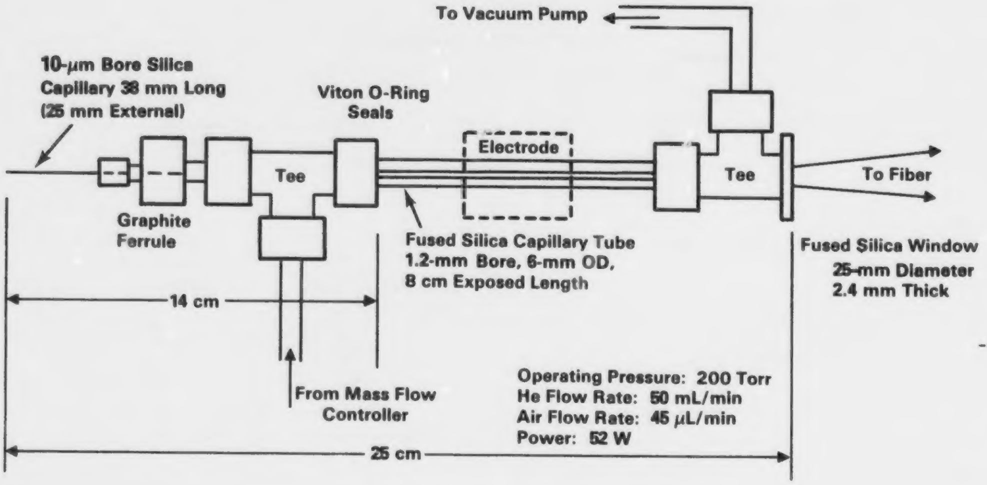

To Vacuum Pump
10-μm Bore Silica Capillary 38 mm Long (25 mm External)
Viton O-Ring Seals
Electrode
Tee
Tee
To Fiber
Graphite Ferrule
Fused Silica Capillary Tube 1.2-mm Bore, 6-mm OD, 8 cm Exposed Length
Fused Silica Window 25-mm Diameter 2.4 mm Thick
14 cm
From Mass Flow Controller
Operating Pressure: 200 Torr
He Flow Rate: 50 mL/min
Air Flow Rate: 45 μL/min
Power: 52 W
25 cm

Figure 1. Schematic Diagram of RFIHP Prototype Probe

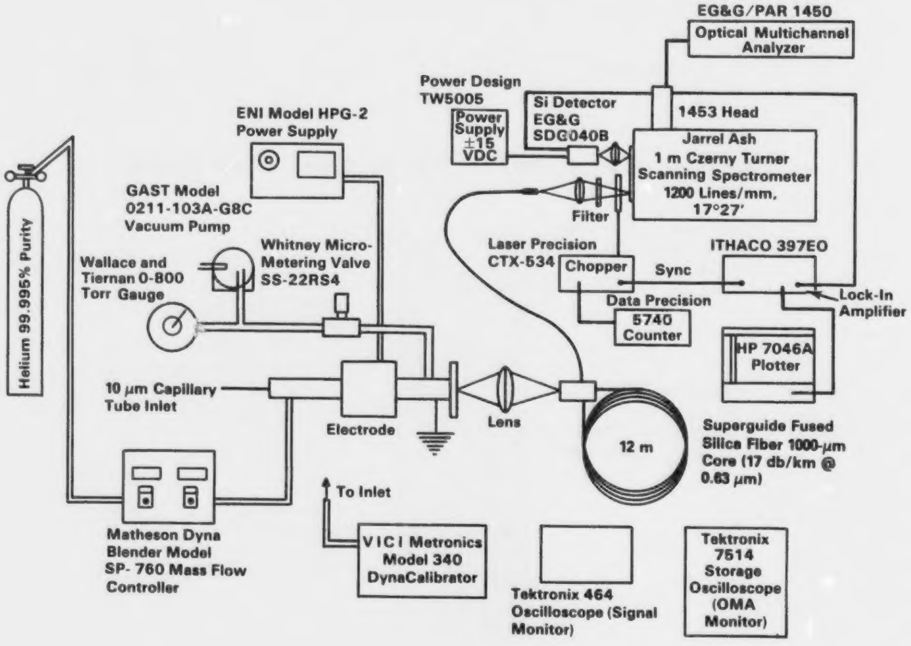
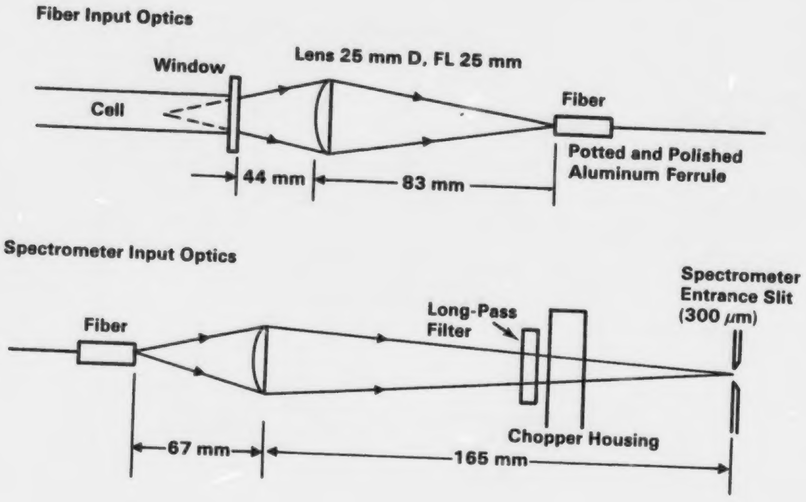

EG&G/PAR 1450
Optical Multichannel Analyzer
Power Design TW5005
Power Supply ±15 VDC
Si Detector EG&G SDG040B
1453 Head
Jarrel Ash 1 m Czerny Turner Scanning Spectrometer 1200 Lines/mm, 17°27'
ENI Model HPG-2 Power Supply
GAST Model 0211-103A-G8C Vacuum Pump
Filter
Whitney Micro-Metering Valve SS-22RS4
Laser Precision CTX-534
Chopper
Sync
ITHACO 397EO
Lock-In Amplifier
Wallace and Tiernan 0-800 Torr Gauge
Data Precision
5740 Counter
HP 7046A Plotter
Helium 99.995% Purity
10 μm Capillary Tube Inlet
Electrode
Lens
12 m
Superguide Fused Silica Fiber 1000-μm Core (17 db/km @ 0.63 μm)
To Inlet
Matheson Dyna Blender Model SP-760 Mass Flow Controller
VICI Metronics Model 340 DynaCalibrator
Tektronix 464 Oscilloscope (Signal Monitor)
Tektronix 7514 Storage Oscilloscope (OMA Monitor)

Figure 2. Schematic Diagram of Experimental RFIHP System



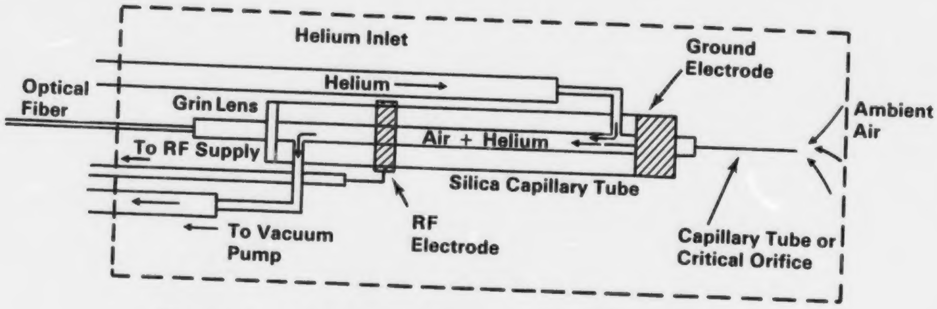
Fiber Input Optics

Window
Lens 25 mm D, FL 25 mm
Cell
Fiber
Potted and Polished
Aluminum Ferrule
44 mm
83 mm

Spectrometer Input Optics

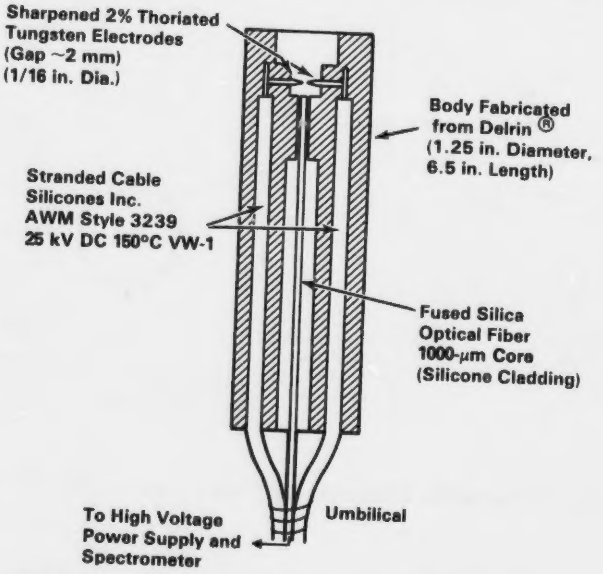
Spectrometer
Entrance Slit
(300 μm)
Long-Pass
Filter
Fiber
Chopper Housing
67 mm
165 mm

Figure 3. Diagram of Input/Output Optics for RFIHP



Helium Inlet
Ground
Electrode
Optical
Fiber
Helium
Grin Lens
Ambient
Air
To RF Supply
Air + Helium
Silica Capillary Tube
To Vacuum
Pump
RF
Electrode
Capillary Tube or
Critical Orifice

Figure 4. Conceptual Design of RFIHP Field Probe



Sharpened 2% Thoriated
Tungsten Electrodes
(Gap ~2 mm)
(1/16 in. Dia.)
Body Fabricated
from Delrin ®
(1.25 in. Diameter,
6.5 in. Length)
Stranded Cable
Silicones Inc.
AWM Style 3239
25 kV DC 150°C VW-1
Fused Silica
Optical Fiber
1000-μm Core
(Silicone Cladding)
Umbilical
To High Voltage
Power Supply and
Spectrometer

Figure 5. Schematic Diagram of SD Probe

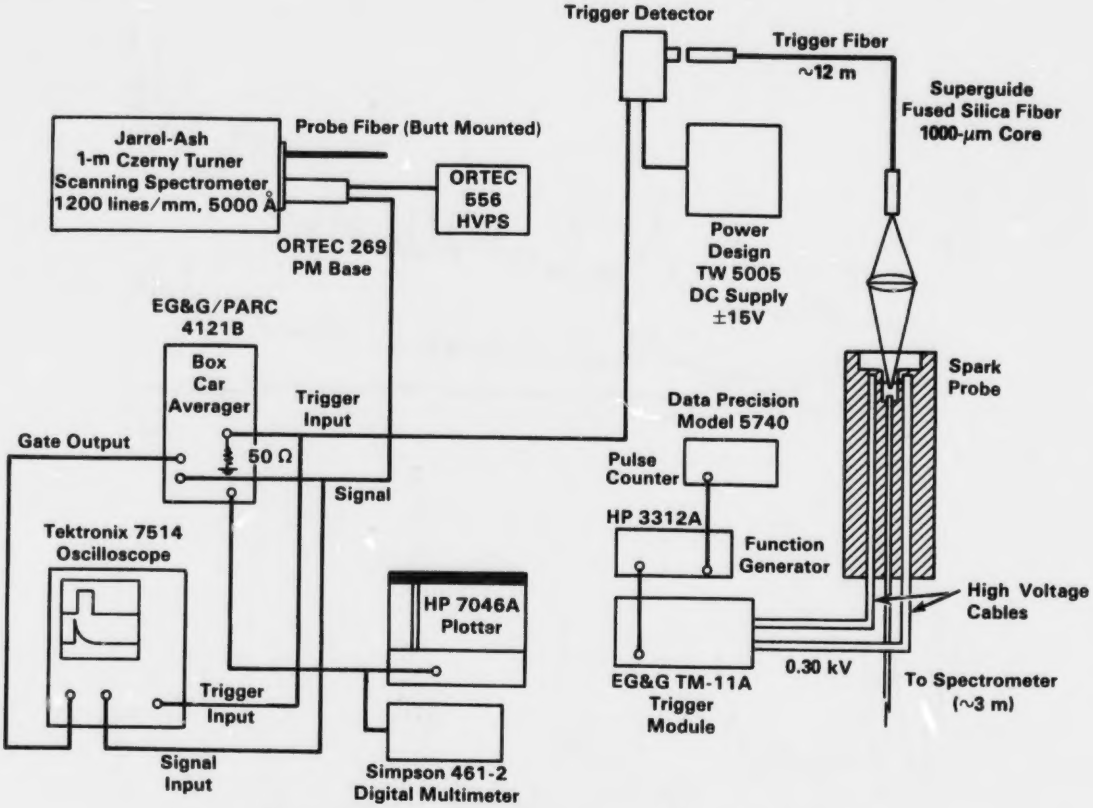

Trigger Detector
Trigger Fiber
~12 m
Superguide
Fused Silica Fiber
1000-μm Core
Jarrel-Ash
1-m Czerny Turner
Scanning Spectrometer
1200 lines/mm, 5000 Å
Probe Fiber (Butt Mounted)
ORTEC
556
HVPS
Power
Design
TW 5005
DC Supply
±15V
ORTEC 269
PM Base
EG&G/PARC
4121B
Box
Car
Averager
Trigger
Input
Gate Output
50 Ω
Signal
Spark
Probe
Data Precision
Model 5740
Pulse
Counter
HP 3312A
Function
Generator
Tektronix 7514
Oscilloscope
HP 7046A
Plotter
High Voltage
Cables
0.30 kV
To Spectrometer
(~3 m)
EG&G TM-11A
Trigger
Module
Trigger
Input
Signal
Input
Simpson 461-2
Digital Multimeter

Figure 6. Schematic Diagram of Experimental SD System

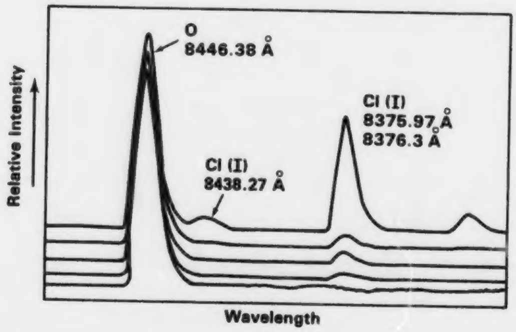


Figure 7. Evolution of Chlorine Emission for Decreasing TCA Concentration

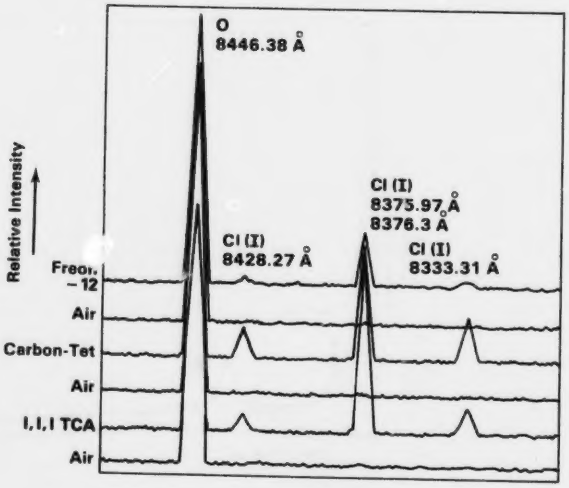


Figure 8. Comparison Response of RFIHP to Three Chlorine-Containing Compounds Versus Air

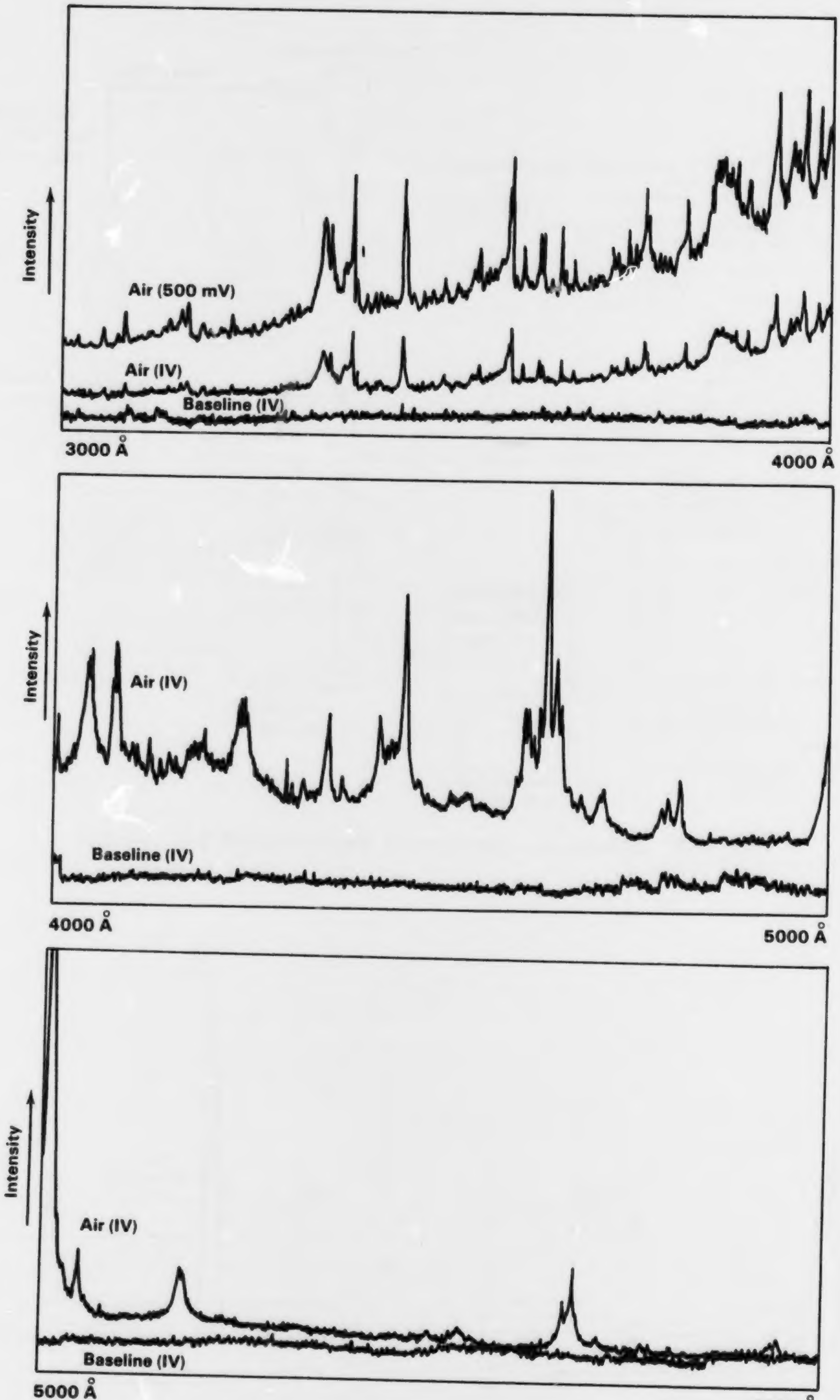


Figure 9. Spark Probe Air Spectra from 3000 to 6000Å
(a) 3000 - 4000Å, (b) 4000 - 5000Å,
(c) 5000 - 6000Å

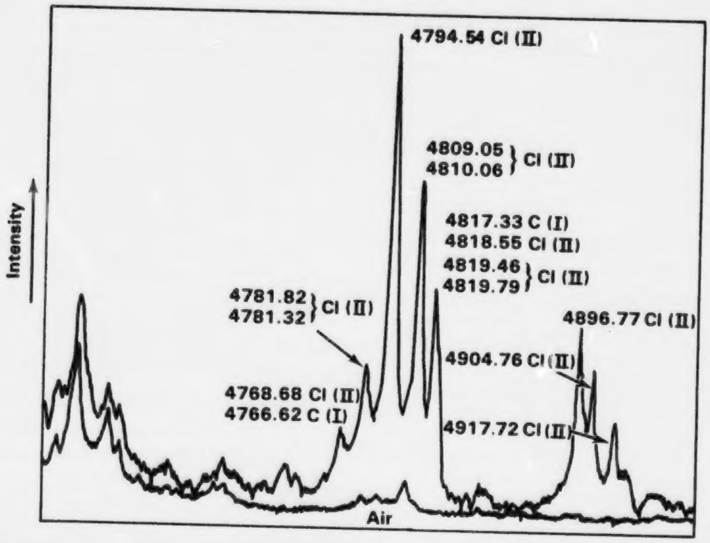


Figure 10. Response of SD Probe to Carbon Tetrachloride Relative to Air

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DISCUSSION

EDWARD HEITHMAR: What was the radio frequency?

KHRIS OLSEN: 276 kilohertz. That's a 9.1 kilowatt power peak to peak.

EDWARD HEITHMAR: Is that self igniting?

KHRIS OLSEN: Essentially, yes. The system that we have has a pulse that ignites it. When there is a high analyte concentration in there, ignition has to be done with a coil.

EDWARD HEITHMAR: So you have a problem with quenching of the plasma with a high analyte, and then having to re-ignite.

KHRIS OLSEN: With the slow leak system, we do not run into that problem, since the amount of liquid or vapor that was present in the gas did not cause any problems. When we saturated the system with air, we had most of our problems. It doesn't like air very much. In other words, if it's saturated with air, at the 10% level, it is slow in igniting. In a helium atmosphere, it goes very quickly.

HANK WOHLTJEN: Is there any reason you didn't go to just a simple platinum wire ionization type sensor to do halogens?

KHRIS OLSEN: No.

POROUS GLASS FIBER OPTIC SENSORS FOR FIELD SCREENING OF HAZARDOUS WASTE SITES

by

S. M. Finger, P. B. Macedo, Aa. Barkatt, H. Hojaji,
N. Laberge, R. Mohr, M. Penafiel

Catholic University of America
Vitreous State Laboratory
Washington, DC 20064

ABSTRACT

Rugged, continuous porous glass fiber optic sensors have been developed and successfully demonstrated for pH and temperature measurements. Porous glass fiber optic sensors are made by selective leaching of a jacketed borosilicate glass fiber. The degree of leaching can be controlled to provide a monolithic structure with a pre-determined pore size which can be varied to allow these sensors to be used for measurements in liquids, gases, or mixed matrices, e.g. sludges. The monolithic structure also maintains the strong attachment between the sensor portion and the rest of the fiber, which acts as a light pipe. Since the sensor is an integral part of the fiber, losses between the sensor and light pipe regions are minimized. The end of the sensor is coated with a thin, porous layer of gold to reflect the incident and response radiation back into the light pipe for analysis.

Porous glass fiber optic sensors can be designed for a wide variety of analytes by changing the active species (or combination of active species for multi-analyte measurements) bonded to the large internal surface area of the sensor. The pH and temperature sensors which were produced used dyes as the active species. However, other active species, such as enzymes and other biochemicals, could be attached to the internal glass surface. Sensitivity can be controlled by varying the length of the porous sensor region and by varying the concentration of the bonded active species. It should also be noted that the light makes two passes across the porous sensing region since it is reflected at the end of the sensor.

A mathematical analysis of a fluorescence sensor was performed. It was found that the sensitivity of a 2 cm long porous sensor would be over 200 times as great as the sensitivity of a two-fiber fluorescence sensor because the porous sensor is able to capture essentially all the fluorescence given off within the fiber. In the two-fiber system (the two fiber tips being tangent and at an angle of 22°), only a fraction of the fluorescence is captured in the receiving fiber; the rest is lost in the open region between the fibers.

The ruggedness, wide applicability and inherent sensitivity of porous glass fiber optic sensors offer significant advantages for the development of low-cost, portable, real-time field screening methods which are critical for effective hazardous waste site evaluation and surveillance monitoring.

BACKGROUND

The demand by the Environmental Protection Agency (EPA) for environmental monitoring data has increased explosively over the last ten years. There are several factors for this increased demand. First, the Agency has moved to expand monitoring coverage from a focus on conventional pollutants to a strong focus on toxic pollutants. Second, the number of matrices has been enlarged from a focus on air and fresh surface water to monitoring coverage of soil, sediment, groundwater, marine water, estuarine water, drinking water, and fish tissue. Third, the number of EPA Program Offices with their own major monitoring programs has also increased dramatically: from air and surface water only, to the establishment of major monitoring efforts for Superfund, Resource Conservation and Recovery Act (RCRA), Toxic Substances Control Act (TSCA), and Safe Drinking Water Act (SDWA).

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The result has been an exponential surge in demand by the EPA Program Offices for new analytical methods to support these monitoring programs and needs. In addition, there is a critical need to reduce the cost of monitoring. This very real problem must have a high priority to ensure that programs addressing critical environmental problems are not delayed or limited due to the high cost of monitoring. These critical and urgent problems will be exacerbated in the future as the Agency highlights new initiatives and intensifies current areas of activity.

To overcome these problems, a new generation of field monitoring methods is required. These methods must be (a) easy to use, (b) inexpensive to operate, (c) real-time, (d) in situ, (e) capable of screening a wide variety of analytes, (f) reliable, (g) rugged, (h) portable, (i) have long shelf lives, and (j) be capable of unmanned operation[1]. Fiber optic monitors have the capabilities to meet these requirements. Fiber optics have been used as a light pipe in spectrometric systems[2-4] and as an integral part of chemical sensors[5-7].

Fiber optic chemical sensors typically have reactive species on the external surfaces of the optical fiber, such as on the tip or outer wall of the fiber, or the fiber is immersed in a reservoir of reagent[1]. The subject of this paper is a fiber optic sensor with an integral porous tip so the optical interaction takes place throughout the volume of the sensing element.

DESCRIPTION OF THE SENSOR

The preparation of the porous glass fiber optic sensor has been described by Macedo, et al[8] and is summarized here. Borosilicate glass optical fiber is made porous by having the fiber go through a phase separation furnace while it is being pulled. This causes the borosilicate glass to separate into a silica-rich and a silica-poor phase. The soft, silica-poor phase is then removed by acid leaching at 90-95 C, which is followed by a long water rinse to remove substances such as silica gel, which precipitate within the pores upon leaching. This process produces glass fibers with pore sizes as small as 40 microns. The active species is then attached by silanization. We have used this procedure to attach a variety of dyes. The dye is covalently bonded to the glass surface through a silane coupling agent which prevents loss of the dye (or other active reagent). Last, sputtering was used to coat the end of the sensor tip with a thin, porous layer of gold. The gold acts as a mirror so that a single optical fiber can be used for both incident and response light transmission. Thus, for example, this design allows for two-pass absorbance measurements. Also, fluorescence measurements can be performed with only one fiber, rather than two, since both the incident and emitted light are transmitted within a single fiber.

The optical fiber with the porous sensor tip, shown in figure 1, is attached via a standard connector to a directional coupler which in turn, is connected to an appropriate source and detector, as shown in figure 2.

Porous glass fiber optic sensors have several advantages over other fiber optic sensors. These include: (a) ruggedness (the sensor element is integrally attached to the fiber wave guide and because the active species is bonded to the interior of the sensor), (b) minimal reflection at the light pipe-sensor interface (the porous tip is integrally attached to the light pipe), (c) effective control of sensitivity (the length of the porous sensor tip can be varied as can the concentration of active reagent on the glass surface within the sensor), and (d) ability to perform multiple simultaneous analyses (the system can provide incident radiation and measure absorbance, fluorescence or raman scattering at several wavelengths at the same time). These features make porous glass fiber optic sensors well-suited for in situ, real-time, remote measurements by personnel with minimal training.

EXAMPLES OF APPLICATIONS

A. Absorbance Measurements

pH and temperature porous glass fiber optic sensors have been successfully prepared. pH sensors used phenol red or cresol red as the indicator dye. Optical absorbance measurements at 575 nm were found to provide a good response to pH changes. Figure 3 shows this response from pH 5 to 8. Figure 4 shows the response of a porous glass fiber optic temperature sensor from 28 to 70 C. This sensor used pinacyanol chloride as the indicator dye; absorbance measurements were made at 625 nm.

Absorbance measurements using dyes would also be effective for monitoring the concentration of heavy metals and chlorinated organics. Beer's Law can be used to estimate detectability limits:

$$A = eLc \tag{1}$$

where A is the absorbance, e is the molar extinction coefficient, L is the length of the porous sensor tip, and c is the concentration of the analyte. Assuming a minimum absorbance measurement of 0.02, a molar extinction coefficient of 2x104 liters/cm-mol, and a porous sensor length of 4 cm, the minimum detectable concentration of analyte would be:

$$Cm = 2.5x10-7 \text{ mol/liter}$$

If the molecular weight of the analyte is assumed to be 100, the minimum detectable concentration could be expressed as:

$$\begin{aligned} Cm &= (2.5x10-7 \text{ mol/L})(100\text{g/mol}) = \\ &\quad 2.5x10-5 \text{ g/L} \\ &= 25 \text{ ppb} \end{aligned}$$

Thus, absorbance measurements in the low ppb range are achievable with porous glass fiber optic sensors. Since there are many dyes which can be used for such sensors, these monitoring devices can be adapted to a wide range of analytes. Also, since the spectral response of the dyes is in the visible range, losses in the light pipe portion of the sensor would be minimal.

The response of the fiber optic absorbance sensor could be optimized for maximum response for a desired concentration range. The intensity of the light decreases in accordance with Beer's Law. Stated in terms of intensity rather than absorbance, the relationship is:

$$I = Io \exp(-eLc) \qquad (2)$$

where I is the intensity of the light as it passes through the sensor region and Io is the intensity of the incident light. Differentiating twice, with respect to concentration and sensor length, gives:

$$\partial 2I/\partial L\partial c = Io(eLc-1)\exp(-eLc) \qquad (3)$$

Setting equation 3 equal to zero to determine the relationship for maximum response, we obtain:

$$eLc = 1 \qquad (4)$$

Equation 4 can be used for maximum response of the sensor for a given concentration of analyte. While it would not be possible get maximum response near detectability limits, this relationship is useful to optimize the sensor at higher analyte concentrations.

B. Fluorescence Measurements

As noted earlier in this paper, fluorescence measurements could be performed using a single porous fiber rather than a two-fiber system as is currently required. In addition to being simpler in design, porous fiber fluorescence systems provide a significant enhancement in signal intensity. This is due to the analyte molecules and the excitation and fluorescence radiation all being contained within the porous sensor. In a two-fiber fluorescence system, the analyte molecules fall in the open region between the two fibers so that only the excitation and emitted radiation within the numerical aperture of the fibers is measured; the rest is lost to the surroundings. The comparison is exemplified by the two situations depicted in figure 5. The angle between the two fibers in Situation I is chosen as 22o and the diameter is chosen as 0.6 mm (as is used in the fluorescence sensor described in reference 2). The fluorescence intensity of the two-fiber system is given by the following equation:

$$\begin{aligned} FI &= [4Ioo/\pi DI^2]\,[f\Omega c]\,[(DI\cos\theta) \\ &\qquad (DI\sin\theta)(2DI)(\pi/4)^2] \\ &= Ioof\Omega cDI(\pi/2)\cos\theta\sin\theta \qquad (5) \end{aligned}$$

where Ioo is the intensity of the incident radiation, D is the fiber diameter, f is the fluorescence efficiency, Ω is the solid angle subtended by the numerical aperture, 2θ is the angle between the two fibers and c is the concentration of analyte.

The fluorescence intensity of the porous glass fiber system is given by the following equation:

$$\begin{aligned} FII &= [4Ioo/\pi DII^2][f\Omega c] \\ &\qquad [(\pi DII^2L/4)(2)(2)(1/2)] \\ &= 2Ioof\Omega cL \qquad (6) \end{aligned}$$

where L is the length of the porous sensor element. Equation 6 takes into consideration the two passes of the incident and emitted radiation through the sensor region. The ratio of the fluorescence intensity between the two systems is given by:

$$R = FII/FI = 4L/\pi DI \cos\theta \sin\theta \qquad (7)$$

Assuming a 2.0 cm length of porous sensor, L, a 0.6 mm fiber diameter, DI, and an angle of 22o between the two fibers in situation I, 2θ, the ratio of the fluorescence intensities between the two systems would be:

$$R = 228$$

This means that the porous glass fiber optic sensor would provide a signal that is over 200 times as strong as the two-fiber fluorescence system! This increased intensity could be used to perform measurements at lower concentration levels, or it could allow the use of an incandescent-source insteadof a more complex but powerful laser source. Either way, the porous fiber sensor would offer distinct advantages over the two-fiber system.

CONCLUSIONS

The ruggedness, wide applicability and inherent sensitivity of porous glass fiber optic sensors offer significant advantages for the development of low-cost, portable, real-time field screening methods which are critical for effective hazardous waste site evaluation and surveillance monitoring.

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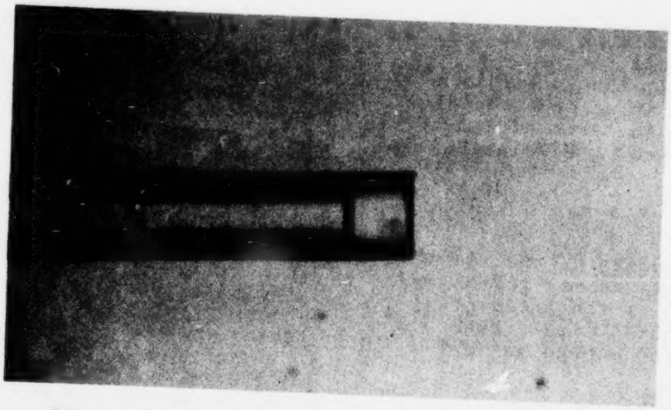


Figure 1. Porous Glass Fiber Optic Sensor

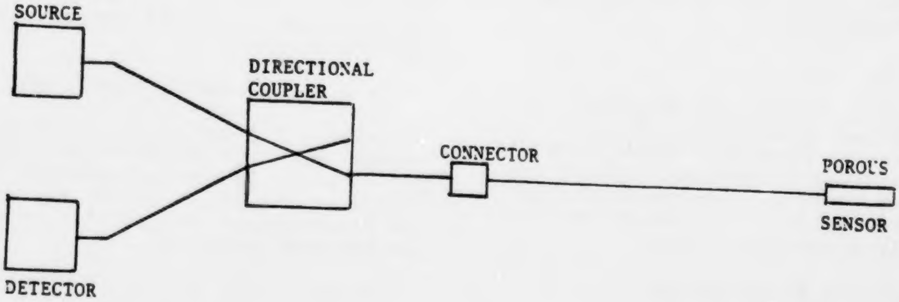


Figure 2. Arrangement of optical components

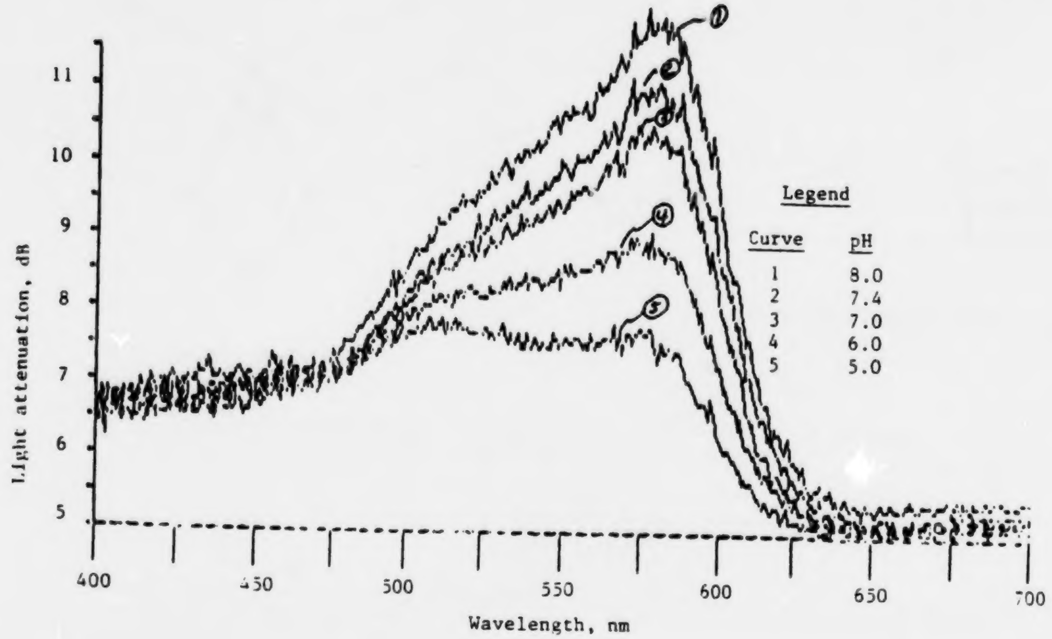


Figure 3. pH porous glass fiber optic sensor response

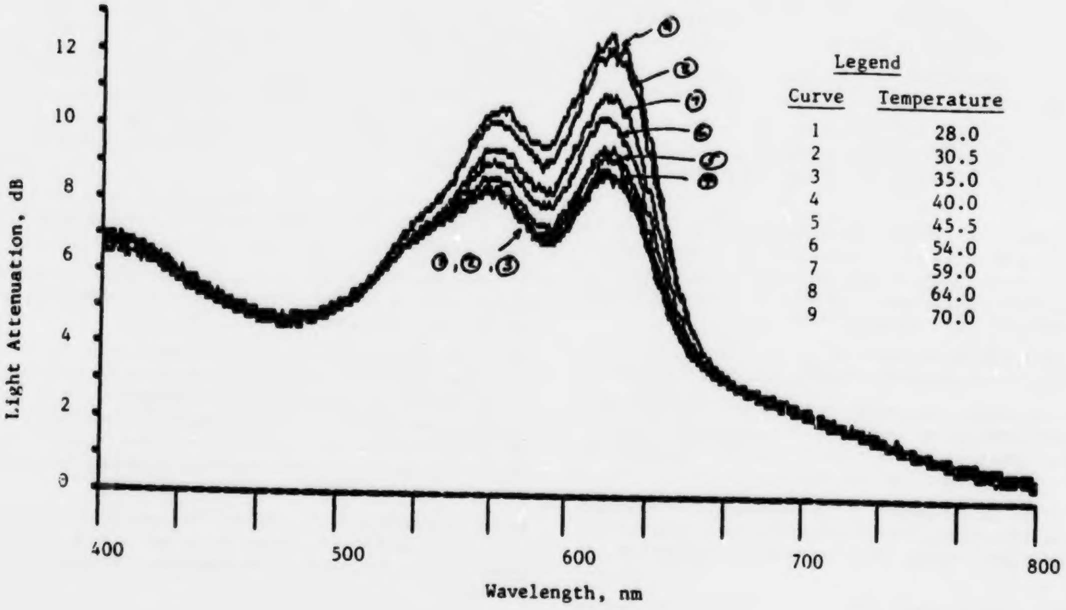
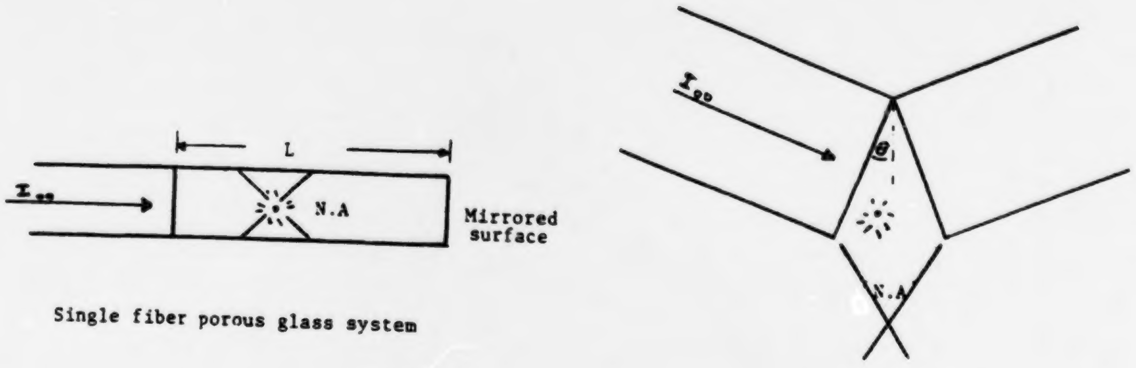


Figure 4. Temperature porous glass fiber oprice sensor response



Single fiber porous glass system

2-fiber system

Figure 5. Comparison of the single fiber sensor vs. a two-fiber fluorescence system

DISCUSSION

DELYLE EASTWOOD: Could you elaborate about the pore sizes, and how you would vary those for various reagents and possible diffusion problems for those smaller pore sizes?

STANLEY FINGER: Pore sizes are quite controllable. We have been able to get down to pores on the order of about 40 to 50 angstroms. Obviously, for the gaseous systems, you can work with the smaller size pores. For liquid systems, you're going to need larger pores, on the order of several hundred angstroms.

The pore size is controlled through the heat treatment itself, and by varying the temperature and residence time of the heat treatment. You can very easily change the pore size. In addition, there are a number of different temperature and time combinations that will give you the same range of pore sizes.

While there is one optimum for any given pore size distribution, you still have a wide range of conditions in which you can get that pore size distribution.

The other factor that comes into the choice of pore size, of course, is the response time. By enlarging the pore size, you improve the response time, because of the smaller diffusion path that's required and the larger diameter for that diffusion path.

So enlarging the pore size is helpful in terms of response times, although we haven't had real problems with that. These sensors tend to come to equilibrium within a minute or two – a fairly quick response. We don't see the need for these sensors to get down to response times on the order of a second or so, although that could potentially be done. We haven't looked at that.

STEVEN GOHEEN: You fused the porous and the nonporous regions of the fiber optic. Did you ever quantitate the difference between fused and unfused?

In other words, it could be cumbersome in the field to have to change the entire fiber optic every time you were measuring a different component, or using a different sensor. Maybe a sensor would wear out, and you want to replace the tip. Did you actually quantitate the difference?

STANLEY FINGER: These sensor tips aren't really fused. They are actually an integral part of the sensor, which is leaching out a portion of that sensor tip. The term fuse implies something with connecting the tip on, and that's not quite correct.

The problem of looking at multi-analytes, relates to whether we can look at a number of different spectral locations at the same time, or use several different dyes at the same time, and the answer is yes.

There is no reason why you couldn't be looking at different portions of the spectrum for different analytes simultaneously, or have more than one dye, or other type of measurement being made at the same time.

The problem of changing these is one of going back to the connector and changing it at that point. The connector doesn't have to be yards, or any great distance away from the tip. You can have a connector fairly close to the tip, if you want to periodically change the sensor tip.

We don't see this as being a problem. In fact, we see it as being one of the advantages of the porous sensor, and periodically changing these as they wear out can be done fairly easily.

HANK WOHLTJEN: The porous glass sensor is a very elegant approach, but there is a fundamental problem with any optical sensor that's based on a colorimetric change of an immobilized reagent. The band shift that occurs is caused by changes in the activity of the medium, rather than the concentration. So you can't really make a pH sensor. You make a sensor that's sensitive to hydrogen ion activity, and not necessarily hydrogen ion concentration. If you have a pure solution of known pH, you can get an accurate measure of it, but if you have an unknown in there that is going to change the ionic strength of the solution, then you can't get an accurate measure. You'll get good data, but what will it mean?

STANLEY FINGER: That is typical with all optical systems, especially dye-type systems, and I don't know that it can be solved completely, except through extensive calibrations for any particular analyte.

You would have to look for a situation where the expected changes in the environment would not significantly change the signal, so that what you are measuring can be related pretty closely to concentration.

Our idea for these sensors is to look at hazardous waste sites in terms of monitoring. The need is primarily to determine whether there is a significant amount of a particular hazardous component. The accuracy of our measurement is less important than perhaps in the standard laboratory test, where you have to take that data and go into court, and fine somebody based upon it. What we're looking at here is do we have a significant amount of concentration – is there a problem here, or not?

HANK WOHLTJEN: By the same token, fluorescence measurements may not have that kind of complication. In your scheme to do fluorescence measurements, how do you strip off the excitation light? Do you use a filter and is it adequate?

STANLEY FINGER: Yes, it's done through the coupler, and the filters, and it is adequate from what we have been able to determine.

INSTRUMENTATION AND METHODOLOGY FOR MULTICOMPONENT ANALYSIS USING *IN SITU* LASER-INDUCED FLUORESCENCE

Jonathan E. Kenny, George B. Jarvis, and Hong Xu
Department of Chemistry
Tufts University
Medford, MA 02155

ABSTRACT

In order to facilitate remote, *in situ* monitoring of multiple contaminants in groundwater, we have improved our prototype laser/fiber optic instrument by the addition of a Raman shifter and a diode-array spectrometer detector. In this paper, we discuss the performance of the Raman shifter in producing multiple excitation wavelengths, the correction of observed spectra for source fluctuations, and related topics.

KEY WORDS: fluorescence, fiber optics, *in situ*, Raman shifter

INTRODUCTION

The sensitivity of the laser-induced fluorescence technique, along with the many advantages of fiber optics for remote sensing, can be combined to produce powerful instrumentation for *in situ* monitoring of groundwater (1). Although the ingenious design of molecule-specific or functional-group-specific optrodes (2) makes it possible to detect even non-fluorescent analytes using fluorescence-based techniques, our work has concentrated on the monitoring of naturally fluorescent species. These include about half of the substances on the EPA's list of 119 priority pollutants.

Recently, we developed a simple, sensitive, and portable instrument which uses the ultraviolet output of a frequency-quadrupled Nd:YAG laser to induce fluorescence in various aromatic molecules in aqueous solution (1). We demonstrated the sensitivity of this instrument to be in the parts-per-billion regime for substances like phenol and unleaded gasoline, when the light was carried to and from the remote sample by a pair of 20- to 25-meter long, 600-μ diameter fused-silica optical fibers (3).

One limitation of this first-generation instrument was its lack of specificity. Since fluorescence detection offers the possibility of considerable specificity, we have attempted to work towards molecule-specific detection in a remote-sensing instrument.

Warner and coworkers (4) have developed and reviewed luminescence-based techniques for identifying specific components in mixtures. Of course, the principle is simple: measure enough parameters of the sample, and you will be able to effect a mathematical "separation" in the computer instead of a physical separation in the laboratory. The most fundamental aspect of molecular luminescence is its dependence on wavelength: the absorption and emission spectra of a molecule provide two characteristic "signatures" by which that molecule may be identified. Our focus will be on the collection and analysis of Excitation-Emission Matrices (EEM's) of pure compounds and mixtures, which contain the encoded spectral signatures of each fluorescent component.

Now we briefly explain EEM's. For a single fluorescing component, the measured fluorescence intensity, M, as a function of excitation wavelength, λ_x, and emission wavelength, λ_m, is given by

$$M(\lambda_x,\lambda_m) = k\ I(\lambda_x)\ \epsilon(\lambda_x)\ \Phi(\lambda_m)\ D(\lambda_m)\ c \qquad (1)$$

where k is a scale factor, $I(\lambda_x)$ is intensity of excitation light delivered by the laser and excitation fiber, $\epsilon(\lambda_x)$ and $\Phi(\lambda_m)$ are the components of the absorption and emission spectra of the compound, $D(\lambda_m)$ represents the efficiency with which the emitted light is transmitted through the detection fiber(s) and detected by the sensing instrument, and c is the quantity of interest, i.e., the concentration of the substance being detected. For a dilute mixture, the total signal is just a sum of such terms, one for each fluorescing component. The EEM of a single component or mixture is a matrix of M values, with λ_x and λ_m being the row and column indices. Since $D(\lambda_m)$ is constant in time for a given instrument, only variations in source intensity, $I(\lambda_x)$, must be divided out from the experimental measurement to allow the EEM to be analyzed. For example, the least-squares method can be used to determine the concentration of each fluorophore present in the sample. Other data filtering and reduction schemes have been developed, including autocorrelation techniques (5) which can be useful for fingerprinting of complex mixtures.

Laboratory-based instruments for EEM analysis generally feature lamp-monochromator sources with good temporal stability which may be easily tuned across the desired range of λ_x's with any desired interval size. When performing remote analyses using uv light and fiber optics, lasers become the only practical sources; unfortunately, they are more difficult to tune and are subject to greater intensity variation, even over short periods of time. The work to be discussed herein relates to a convenient, multiple-wavelength excitation source based on stimulated Raman scattering, and a methodology for monitoring laser power fluctuations.

INSTRUMENTATION

A schematic of the instrumentation used for remote multidimensional fluorescence measurements is shown in Figure 1. A Nd:YAG laser (Quanta-Ray DCR-11) with second-, third-, and fourth-harmonic generating crystals is the primary excitation source; its output at 1064, 532, 355, or 266 nm may be used directly, or Raman shifted to produce various other wavelengths. The desired wavelength is chosen by rotating the Pellin-Broca prism at the Raman shifter output; this directs the beam through a variable attenuator and a focusing lens onto the tip of the excitation fiber, which delivers it to the sample. A beamsplitter before the excitation fiber directs a fraction of the light onto a monitoring detector. Fluorescence from the sample is carried to the diode-array spectrometer (Aries Monospec-27) by one or more detection fibers. The EG&G blue-enhanced OMA detector is interfaced to a Compaq 386-20 computer via an IEEE-488 bus.

GENERATION OF MULTIPLE EXCITATION WAVELENGTHS

To overcome fiber transmission losses in the ultraviolet, where many fluorescent compounds must be excited, laser sources must be used. For single-wavelength excitation, we have found a frequency-quadrupled Nd:YAG laser to be convenient: its good power, simple and troublefree operation, and air cooling make it a viable source in a portable instrument. To generate EEM's, multiple λ_x's are needed in the range ≃250-500 nm. In general, the amount of vibrational structure in the absorption spectra of the target molecules dictates the spacing of these wavelengths; intervals of 2-5 nm are typical in laboratory work done in nonpolar organic solvents, while larger intervals should suffice in aqueous solution. The only practical laser sources for generating the required excitation wavelengths in the uv are frequency-doubled dye lasers and Raman shifters (6).

Dye lasers offer considerable advantages: high power, good beam quality, and continuous tunability over a wide spectral range. However, they are fairly complicated and expensive, and, to cover a wide spectral range, several dye solutions are required. Furthermore, to access the shortest wavelengths needed, e.g., 250-350 nm, the output of the dye laser itself must be converted by frequency-doubling.

Raman shifters, on the other hand, are extremely simple, having only one moving part (a tuning prism) and one working fluid. As dye lasers work on the principle of stimulated fluorescence, Raman shifters work on stimulated Raman scattering. Thus, unlike dye lasers, whose output is continuously tunable over some part of the fluorescence spectrum of the dye, Raman shifters produce output only at fixed frequency shifts from that of the pumping laser. Output frequencies occur at intervals of ±1, ±2, ±3, etc., times a fundamental vibrational frequency of the fluid in the Raman shifter. If a Nd:YAG laser with its various harmonics is used as a pump laser, the shifted outputs from each of the inputs provide reasonable spectral coverage, even if only a single working fluid, like H_2 gas, is used. Additional output wavelengths may be obtained by using a second gas; both may be present at once, so no fluid changes are required during tuning.

The output power in each of the available excitation wavelengths from such a system can vary greatly; however, for a reasonably compact Nd:YAG laser pump, and using only H_2 in the Raman shifter, we have generated 21 different wavelengths in the region from 220 to 532 nm having sufficient intensity for remote sensing work, as shown in Figure 2. We are currently studying the effect of using a mixture of H_2 and methane; limited results using this mixture were reported elsewhere (7), and the system looks promising.

MONITORING SOURCE INTENSITY CHANGES

As shown by Eq. 1, the intensity of the observed signal is directly proportional to the intensity of excitation light, $I(\lambda_x)$, *incident on the sample*. The removal of this unwanted dependence in quantitative work is often called power normalization; $I(\lambda_x)$ is measured and both sides of Eq. 1 are divided by the reading to produce a quantity proportional to concentration, c. In conventional fluorimetry, a beamsplitter normally splits off part of the excitation light beam at a suitable point and directs it towards a detector. For *in situ* measurements, there are a number of complications to this simple procedure. First, the focal spot of the laser beam is likely to be highly nonuniform in intensity distribution. Since it is being focused onto a small fiber, care must be taken that an exactly corresponding portion of the split-off focused beam hits the power normalizing detector. Obviously, the second, related problem is to eliminate any vibration or other motion that might cause misalignment, once it is achieved. Third, the attenuation of the excitation fiber varies greatly with wavelength, and this variation must be properly accounted for. Manufacturers' data or actual attenuation measurements could provide this information; however, the transmission properties of fibers which carry large amounts of uv light are known to change considerably over the period of exposure (so-called "solarization").

We have found that these problems may be addressed by monitoring scattered excitation light returning through the detection fiber(s), *in addition to* the measurement of excitation intensity at the source, as described above. The actual experimental work was done using our undispersed-fluorescence detection system, but the principle is equally applicable (and probably easier to implement) in the diode-array spectrometer system used to collect EEM's.

For these power normalization experiments, two changes were made to the block diagram of Figure 1. A Laser Precision joulemeter was put behind a transparent sample holder (a fused silica cuvette filled with distilled water) to monitor the true source intensity reaching the sample. In place of the diode array spectrometer, a detection module (1) was used which could separately monitor total fluorescence and 266-nm Rayleigh scattering. The responses of the pre-launch laser power monitor and the detection module's Rayleigh scattering monitor were measured against the true source intensity at the sample. The results showed good linearity over a suitable range of excitation energies, as depicted in Figure 3. Further details of this experiment and related experiments are given elsewhere (8).

Having demonstrated the viability of using either monitoring scheme for power normalization, we now discuss the rationale for using *both*. The pre-launch reading indicates directly the performance of the laser-Raman shifter system. The Rayleigh monitor directly indicates the performance of the entire instrument. Proper readings on both indicate a functioning system even in the absence of any fluorescence signal (should such a pristine aquifer be located in field work). This is a factor of major importance in a field instrument which may very well be operated in a mode wherein permanently installed fiber optics probes, inaccessible to the operator, are periodically serviced by a mobile instrument. Before a probe is first installed, the initial relationship between the two power normalization channels should be established with the probe immersed in distilled water. Under normal conditions, the Rayleigh probe's reading should be used for actual fluorescence intensity corrections, since it more accurately measures power incident upon the sample as the excitation fiber ages. A comparison of the two readings, in fact, allows solarization of the excitation fiber to be monitored. Thus, the Rayleigh probe ensures that proper source intensity corrections are made throughout the useful life of the excitation fiber, as well as indicating when that useful lifetime has been reached.

Of course, either near-zero or excessively large readings on the Rayleigh monitor indicate conditions under which other types of corrective action must be taken (8).

SUMMARY

The Raman shifter appears to be a promising source for the production of multiple excitation wavelengths, although a two-gas mixture may have to be used as the working fluid to produce a sufficiently fine grid. The proposed power-normalizing scheme, which utilizes two separate measurements, has the additional advantage of providing a means of instrument self-check and monitoring of the solarization of fibers which deliver high-power uv light to the remote sample.

ACKNOWLEDGMENT

We wish to acknowledge the financial support of the U.S. Environmental Protection Agency through a grant to the Center for Environmental Management at Tufts University.

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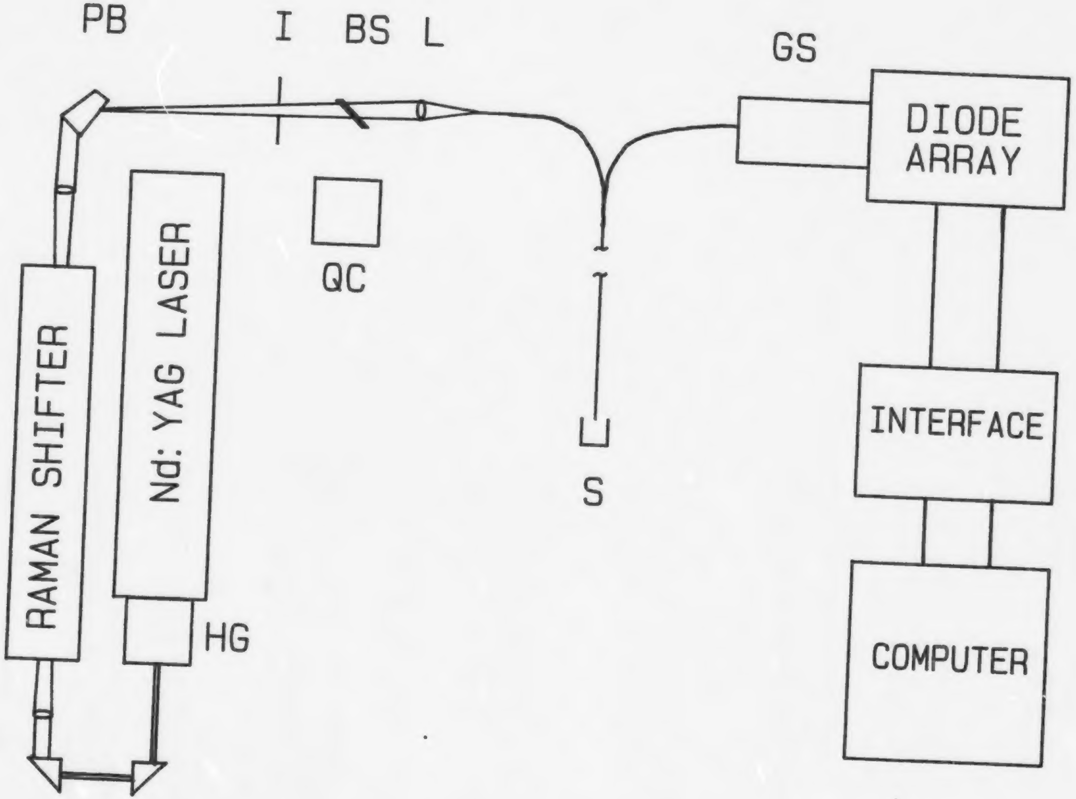
PB
I
BS
L
GS
DIODE ARRAY
QC
RAMAN SHIFTER
Nd: YAG LASER
HG
S
INTERFACE
COMPUTER

FIGURE 1. BLOCK DIAGRAM OF MULTIDIMENSIONAL LUMINESCENCE SPECTROMETER FOR IN SITU MONITORING. HG=HARMONIC GENERATOR, PB=PELLIN-BROCA PRISM, I=IRIS, BS=BEAMSPLITTER, QC=QUANTUM COUNTER LASER MONITOR, L=LENS, S=SAMPLE AND GS=GRATING SPECTROMETER.

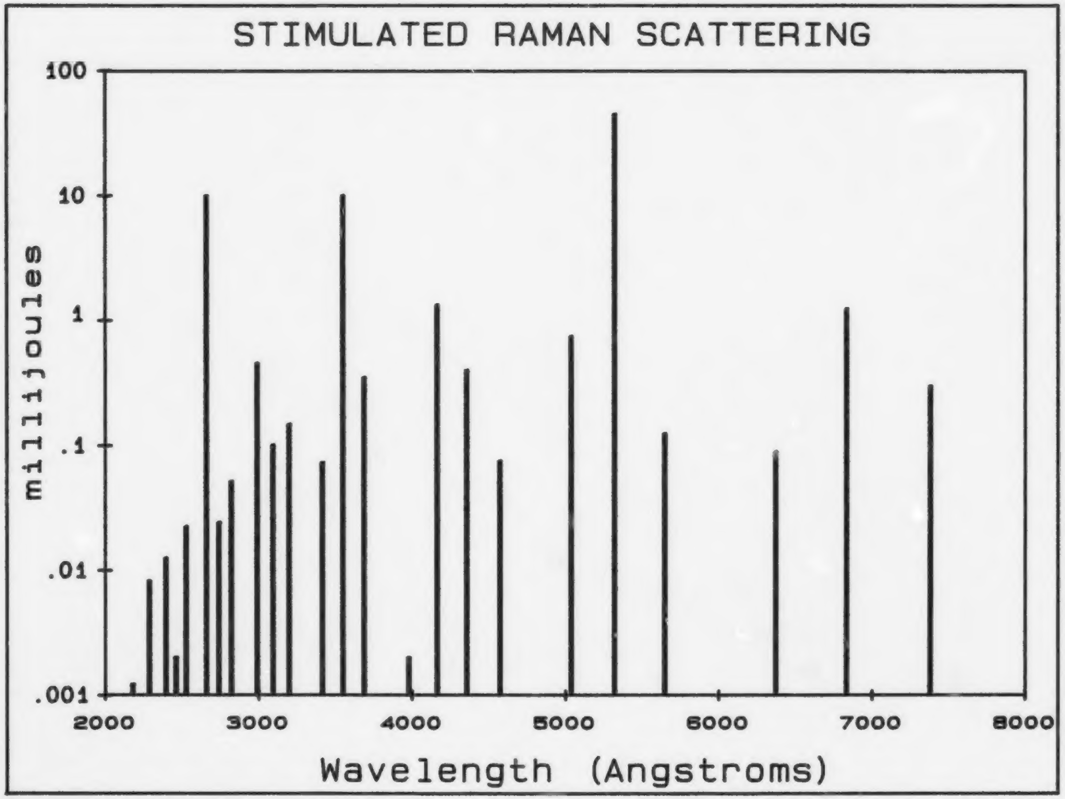

FIGURE 2. OUTPUT OF 200 psig HYDROGEN-FILLED RAMAN SHIFTER PUMPED BY HARMONICS OF YAG LASER

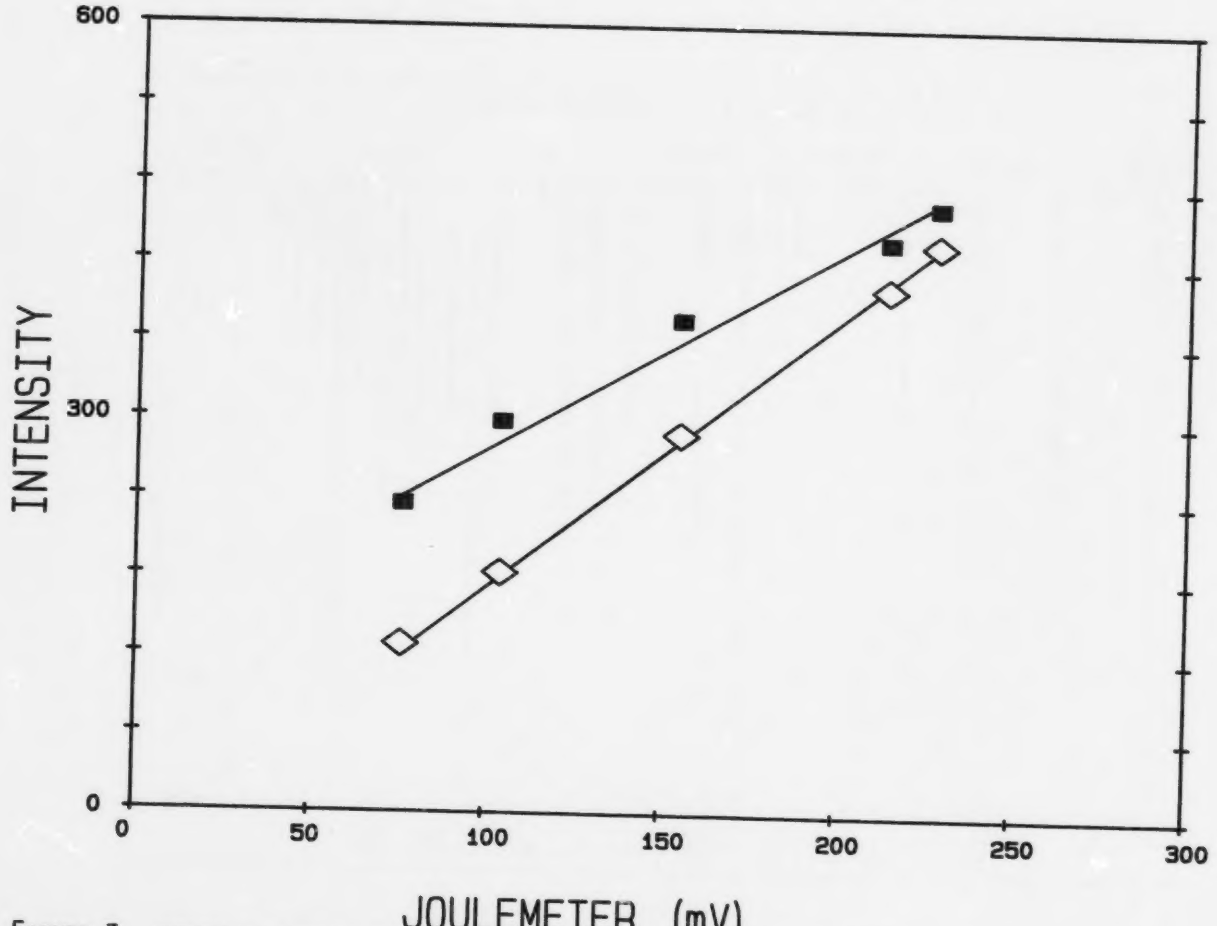

FIGURE 3. RESPONSE CURVES FOR THE TWO LASER POWER MONITORS VERSUS JOULEMETER READING AT THE SAMPLE. DIAMONDS REPRESENT THE PRE-LAUNCH (QUANTUM COUNTER) MONITOR: SQUARES, THE RAYLEIGH MONITOR.

DISCUSSION

DELYLE EASTWOOD: The excitation emission matrix approach which, as you pointed out, largely developed by Christian and Morner, is really more applicable to diagnostic purposes than to monitoring.

When I was with the Coast Guard, we found that we had so much extra data it was confusing.

Isiah Warner and Steve Fuh do have a fiber optical multi-channel analyzer, capable of excitation emission matrices already. I don't remember what laser they used.

UNIDENTIFIED PARTICIPANT: How does the excitation matrix approach account for energy transfer interferences among the competing fluorophores?

JONATHAN KENNY: It really doesn't. The limitation of this approach is that it will work in dilute solutions, and if the solutions are dilute enough, the chromopores don't interact. So it's predicated on the assumption of Beers law for linearity and additivity.

MIKE CARRABBA: We saw earlier this morning a slide by Professor Chudyk, in which he compared the GC/MS data to his data. There were instances where there were two to three order of magnitude differences.

Do you think that that could be accounted for in the power normalization scheme that he is using, versus the one that you're using?

JONATHAN KENNY: The slide he showed of the detection unit looked just like the slide I showed. I think that what might happen is if you're in a nondilute environment, the absorption of some of the scattered light before it gets back into the RLIF probe could be hurting you. It's hard to speculate. I really don't know.

INFLUENCE OF NATURALLY OCCURRING VOLATILE COMPOUNDS ON SOIL GAS RESULTS

by

Royal J. Nadeau
U.S. Environmental Protection Agency
Environmental Response Team
Edison, New Jersey

Joseph Tomaszewicz
ERT Technical Assistance Team
Edison, New Jersey

ABSTRACT

Naturally occurring volatile compounds are present in the vadose zone particularly in soils of high organic content. These compounds are the product of living plants or degradation of plant parts. Some of these compounds have the same retention times as some common hydrocarbon pollutants, producing false postive results.

Knowledge of the types and levels of these naturally occurring compounds is important to the soil gas analyst to make accurate analytical interpretation of chromatographs particularly from portable gas chromatographs.

INTRODUCTION

Soil gas surveys are being widely used to determine the presence of contaminants in the groundwater and overburden materials. Many times these surveys will require collecting soil gas samples in heavily vegatated areas that are believed to be out of the contaminated zone. Often the samples collected from these areas are considered free from volatile contaminants but yet contain many volatile compounds that are present in the soils from natural origins.

Some of these naturally derived volatile compounds possess similiar physical chemical characteristics to certain volatile contaminant compounds. Under these conditions, the analyst using a field detection instrument eg. hand-held total volatile organic detector or portable gas chromatograph could make a false positive determination for that sample.

We have encountered a number of naturally volatile compounds in a number of the soil gas surveys that were performed at sites across the country. This paper will dwell upon these compounds and the problems that were presented to the analyst and data interpretor.

METHODOLOGY:

The method utilized for obtaining soil gas samples consists of creating a 1.5cm diameter vertical hole in the ground using a slam bar followed by inserting a .75cm diameter O.D. stainless steel probe into the hole, sealed at the top with modeling clay. The hole is evacuated for one minute to remove atmospheric infiltration using an air sampling pump. A total organic volatile detector (HNu Model PI101) was then attached to the stainless steel tube to provide a gross level of the total volatile organics present. Following this determination, a sample of the soil gas was collected into a 1.0 L Tedlar bag.

The bagged samples were then analyzed within 24-36 hours from time of collection using a portable gas chromatograph (Photovac Model

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10A10 or 10S50) equipped with a packed column and a photoionization detector (10.7 eV)(GC/PID). Compound identification was made by matching retention times and area responses with external standard gas mixtures composed of selected aromatic and chlorinated hydrocarbons. Syringe blanks were run between each analysis to ensure against carryover contamination. After the Photovac analyses, selected samples were then adsorbed on Tenax/Carbon Molecular Sieve (CMS) tubes for compound identification by GC/MS analysis. One of the criteria for selecting samples for confirmation was the presence of compounds that were not readily identified by the Photovac. These sample tubes were analyzed by thermal desorption onto a cryogenic trap, then analyzed by a Hewlett-Packard 5993 GC/MS using "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" (EPA 600/4-84-041, Apr. 1984).

CASE STUDY #1. (Methane Site)

Explosive levels of a combustible gas determined through the use of a Combustible Gas Indicator Meter (CGI) and Organic Vapor Analyzer (OVA) had been found in the basements in several homes in a new housing development. Some of the homes had been constructed adjacent to subsurface trenches filled with surface vegetation eg. trees, understory shrubs cleared for development (Figure 1.)

Soil gas samples were collected at several locations in the backyards of the homes that were closest to the trenches. Additional soil samples were collected in back of homes that had been constructed in another part of the development. Off-site samples were collected in the backyards of several residences that were not part of the development to determine background levels for the survey.

The field survey data indicated the presence of high concentrations of organic volatiles in the soils with methane comprising most of the organics in the soils behind the homes closest to the trenches. The backyards of those homes used as background samples contained very low or non-detectable levels of organic volatiles.

A Century OVA - 128 was used in the gas chromatographic mode for the methane analysis. The OVA in the gas chromatographic mode produced results that were consistent with the field data; the locations that had high concentrations as measured by the field instruments had high concentrations of methane in the bag samples.

Analytical results from the various analytical tiers used at the Methane Site are presented in TABLE 1. The confirmatory analysis from the GC/MS revealed the presence of low molecular weight hydrocarbons at many locations throughout the site. These low molecular weight hydrocarbons along with olefinic hydrocarbons have been detected in soils by previous investigators and are thought to be the result of microbial activity (Francis et. al.,1975). Terpene isomers were identified at several locations, however the highest concentration was observed at the location with the highest concentration of methane.

CASE STUDY #2. (Chlorinated Solvent Site)

Previous sampling efforts had determined the presence of various chlorinated hydrocarbon compounds in private residential wells (e.g. 1,1-dichloroethane, 1,1,1-trichloroethane and dichloroethylene). The area of concern contained two aquifers, a shallow overburden and a deeper bedrock aquifer. The residences in this area were situated along a north-south roadway with a riverbed located approximately 100 feet to the east. Most houses were on the east side of the roadway with several businesses located west and south of the area. A soil gas survey was conducted to better define the contaminated areas and potential sources.

Analysis of the GC/PID field data did not detect the presence of the expected chlorinated hydrocarbons. TABLE 2. contains the results of both the field PID

TABLE 1. NATURALLY OCCURRING VOLATILE ORGANICS AT METHANE SITE -- SEPTEMBER 1987

LOCATION chemical name	trip blank	No. 22	No. 1	No. 11	No. 8	No. 10	EAST OF TRENCH
acetaldehyde (1)	ND	.013	.008	.011	bmdl	.037	bmdl
terpene isomer (1)	ND	.037	ND	ND	.086	.140	ND
terpene isomer (1)	ND	.031	ND	ND	.018	.053	ND
methane (2)	ND	207	ND	631	>112000	361	>40000
Total Volatile Organics (3)	NR	11	0.5	4.0	.4	105	NR

(1) = GC/MS (in ppm)
(2) = OVA (in ppm)
(3) = HNu Portable Photoionization Detector (in ppm above background as benzene equivalents)
ND = not detected
NR = no reading
bmdl= present but not quantifiable

TABLE 2. NATURALLY OCCURRING VOLATILE ORGANICS AT CHLORINATED SOLVENT SITE SEPTEMBER 1986

LOCATION chemical name	scan	EW-5 ppb	H-16 ppb	G7E1 ppb
terpene isomer	319	2000	3200	1100
terpene isomer	350	ND	550	ND
terpene isomer	382	780	2500	67
terpene isomer	394	ND	ND	760
terpene isomer	414	ND	160	ND
terpene isomer	421	ND	ND	63
terpene isomer	458	ND	ND	140

The GC/MS analysis indicated the presence of aromatic hydrocarbons as observed by the field GC as well as various C_6 - C_{10} alkanes and C_3 alkyl benzenes. The appearance of this mixture of compounds can be indicative of the presence of petroleum distillates and was possible considering the proximity of one transect (G) to a defunct gasoline station and the other transect (R) along the railroad line. The sample points that indicated significant HNu PID readings, but did not show any of the target compounds by field GC did contain four major unknowns. These non-target compounds were identified in the GC/MS analysis as several terpene isomers. The terpene compounds could be expected in areas where coniferous vegetation is present. In fact, a reference was made in a field log indicating the presence of pine trees along a portion of the EW transect. No attempt was made to further identify the specific terpene isomers.

DISCUSSION

It is commonly accepted that naturally occurring volatile organic compounds can influence soil gas measurements (see Table 3.) Direct readout field instruments that measure total volatile organics are likely to include certain naturally occurring compounds along with the anthropogenic compounds of interest.

Some portable instruments with photoionization detectors can be equipped with specific lamps that are not sensitive to the presence of some naturally occurring volatiles but will include others if present. For example, an instrument used at both these sites was equipped with a 10.2 eV lamp that does not detect low molecular weight paraffins (eg. methane, ethane, propane) but is sensitive to certain aliphatic aldehydes and ketones (eg. acetaldehyde, propionaldehyde and acetone) and certain olefins (eg. propylene, ethylene). Some investigators have found concentrations of ethylene at greater than 20 ppm in soil gas in saturated soils under anaerobic conditions[5]. A perched water table was present at the Methane Site (Figure 2.) at those locations where the highest concentrations of methane was observed.

Although the presence of ethylene was not confirmed by the GC/MS, soil conditions were optimum for its production in addition to the methane.

The presence of terpene isomers in the soil gas at the Chlorinated Solvent site in conjunction with the conifers substantiates the observations of previous investigators. More terpene isomers were observed at this site than at the Methane site. This can attributed to the difference in arboreal species (hardwords at the Methane site versus conifers at the Chlorinated Solvent site). Higher concentrations of terpenes were observed at the Chlorinated Solvent site also

CONCLUSIONS

The presence of naturally-occurring volatile compounds can influence the results of soil gas surveys. Although each naturally-occurring compound may be present in small amounts, when composited, these compounds can influence the total volatile organic level. Caution should be exercised in using total volatile organics as an indicator of pollutant levels present especially at those sites where naturally occurring volatile compounds are abundant. Using total volatile organic level as a measure of pollutants in soils should be done only in those situations where naturally-occurring volatile compounds do not influence the results.

It is especially prudent in those surveys designed to delineate groundwater contamination to incorporate instrumentation that can differentiate between the contaminants and naturally occurring volatile compounds present.

Determining background levels of naturally-occurring volatile compounds is extremely important for characterizing their potential influence on the utility of soil gas results.

ACKNOWLEDGEMENT

The authors express their appreciation for the technical support provided by Alan M. Humphrey, Project Leader for the Chlorinated Solvent site study and to TAT members, Brian McGeorge and Carl Armbuster for their analytical support. They also thank the peer reviewers; Dr. Thomas Spittler, EPA-Region I and Dr. Joseph Lafornara, ERT Team Leader for their helpful comments.

TABLE 3. Naturally Occurring Volatiles released from biological sources.
SOURCE: Stotzky and Schenck, 1976.

COMPOUND	SOURCE	VAPOR PRESSURE*
monoterpenes (C_{10})	conifers (pines)	
(eg. a-pinene,		3.85
b-pinene,		2.81
limonene	aromatic shrubs (eg. *Salvia* & *Artemisia*	1.49
myrcene		
camphene		1.99
sesquiterpenes (C_{15})	conifers and deciduous trees	
alcohols	corn and sunflowers (anaerobic conditions)	
(eg. 1-butanol)		5.0
2-butanol		12.6
isopropanol		26.8
t-butanol		29.9
ethanol		38.6
naphthalenes	potato	0.06
formaldehyde	germinating seeds of a variety of plant types	3366.0
acetaldehyde		748.3
propionaldehyde		257.5
acetone		185.6
ethylene		*******
propylene		7600.
formic acid		31.8
terpenes	dead woody plants	
aldehydes (<9 carbons)		
alkanes (<11 carbons)		
(eg. undecane)		.4
alcohols		
ethylene	anaerobic/aerobic metabolism	
aliphatic aldehydes		
and alcohols		
methylated heavy metals	fungi (mostly) some bacteria	
eg. mercury, selenium,		
tellurium and arsenic		
hydrogen cyanide		

* vapor pressure expressed in mm Hg as extrapolated from several sources. (see literature citations).

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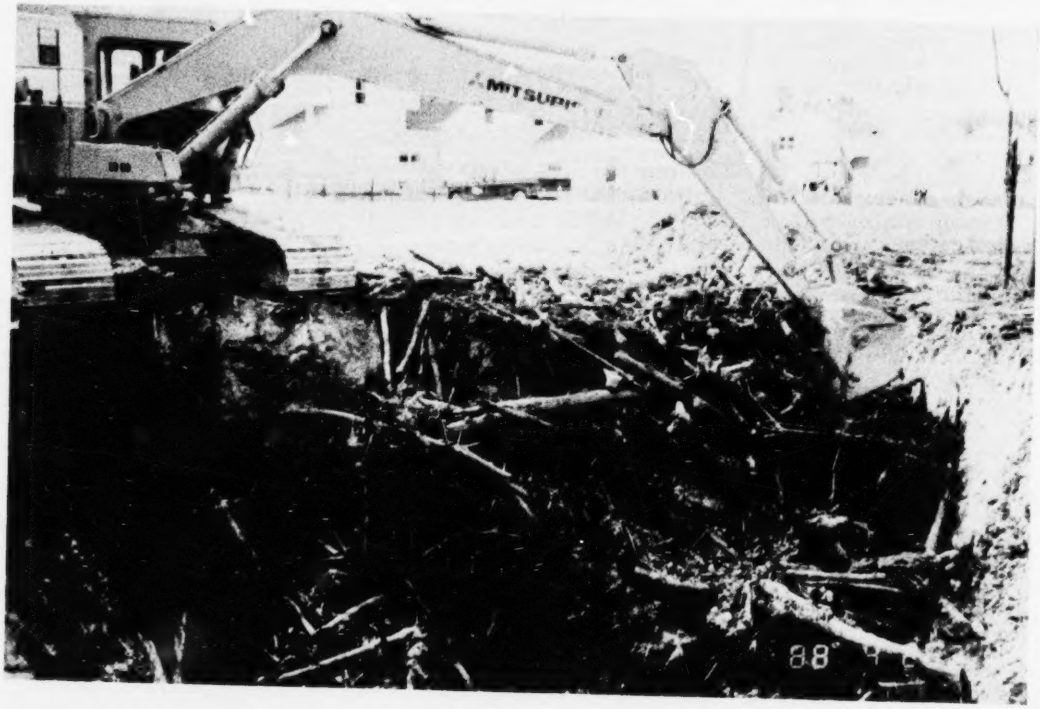

Figure 1 Buried Vegetation at Methane Site

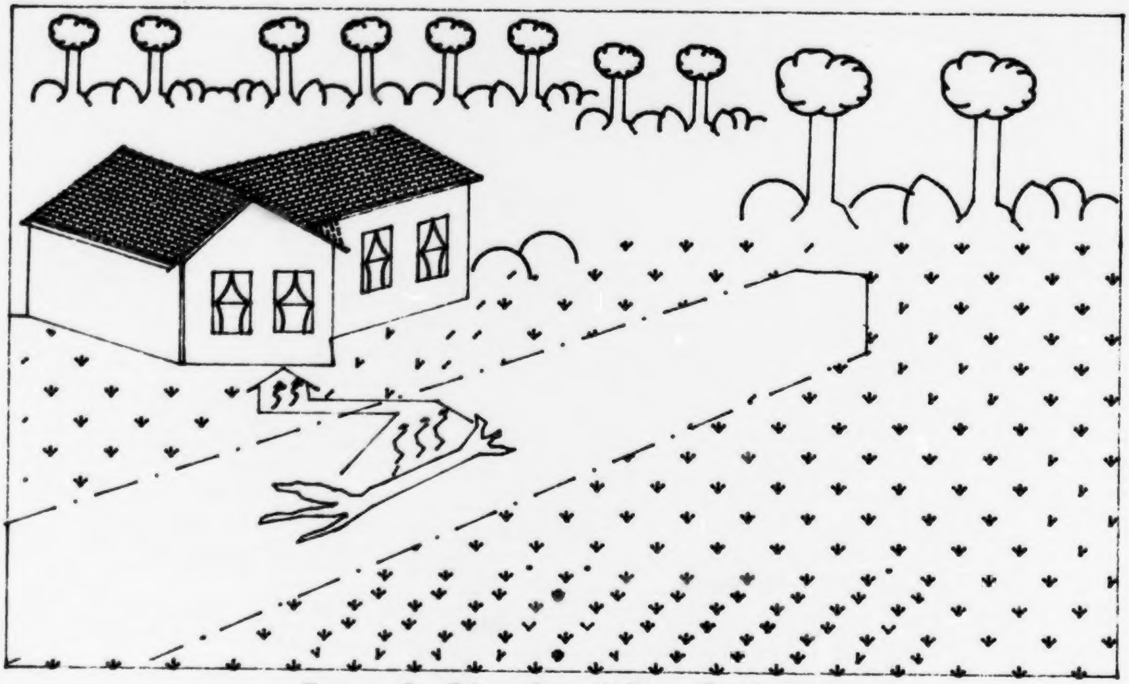

Figure 2. Subsurface Methane Production

DISCUSSION

JONATHAN NYQUIST: Have you noticed when working with high methane, a small negative peak at the beginning of your Photovac chromatogram? We've spotted this, and learned that although methane cannot be detected by a PID detector, methane is a UV absorber, and it will reduce the response to the detector while it's going through.

ROYAL NADEAU: In relation to that, the HNU sometimes goes negative when you are working in areas where methane is likely to be present. This is similar to your situation, because the same type of detector system is present in the HNU as is in the Photovac.

JONATHAN NYQUIST: We found that it can actually lower the response of the HNU, or the Photovac tip to other compounds, because methane becomes part of the carrier gas and knocks down the instrument response.

ROYAL NADEAU: That's a very good point, and one I didn't emphasize, but the matter of coelution is very real with these. It's not just a masking that could take place, if you have a lot of natural compounds present.

JACK McLAUGHLIN: Regarding the picture of performing soil gas in the snow, is this really practical, because of the cold weather, and the lack of volatilization of some of the volatile organics?

ROYAL NADEAU: Obviously, working in a snow-covered field, where you have a frost cover, is not ideal for doing soil gas. It beats the mosquitoes, but it has its drawbacks.

We have been taking temperatures throughout a lot of our soil gas surveys, and once you get three or four feet below the frost zone, you will find there is amazing consistency, that the soil is warmer than you would think.

For instance, I have done soil gas in Colorado, in December and January, and found it was 54°. So if something is there, you will find some volatilization. Of course if your probe isn't long enough to get through the frost zone, you will not be able to collect much of these volatiles in the sample, which will influence your results, especially if you're trying to track a groundwater flow.

JACK McLAUGHLIN: Are you aware any work done on some kind of peripheral device that would heat the zone, so that you could actually take a measurement in the particular zone, if you were down at three or four feet.

ROYAL NADEAU: We have been doing some work in Edison, using electroprobes to heat up a zone. It takes so much electrical energy since the soils are such poor conductors, that you'll end up fusing the soils to form silica before you will get much of a zone to sample. I have heard of some people trying to use steam stripping – injecting steam into the soils with the idea of then trying to drive out the volatiles – so that we're not limited by the time of the year for soil gas surveys.

TOM SPITTLER: When the ground is frozen, you actually have conditions more favorable to doing a soil gas survey, if you keep in mind what the principle focus of the soil gas survey is – to find out whether the vapor in the soil is higher at one place than in another, since it reflects the volatile contamination underground – the underlying material – whether it's a plume or a spill.

With the frozen ground, you basically place a cap on the loss of vapor through the soil, and as a result, you end up concentrating the vapor in the vadose zone, so that you can get a more sensitive reading of what's down there on the water table.

The temperature differences are negligible, because once you're below the frozen surface, you're not experiencing winter time temperatures, you're experiencing normal soil temperatures, which don't fluctuate more than five degrees throughout the year.

So in a sense, it almost enhances a soil gas survey, because you don't get that constant loss through the porous surface of the soil.

ROYAL NADEAU: In addition, groundwater is usually fairly consistent in temperature, so if there are volatiles, they will be coming out of the groundwater.

AN IN SITU TECHNIQUE FOR MEASURING SOIL-GAS DIFFUSIVITY

P. M. Kearl[1], T. A. Cronk[2], and N. E. Korte[1]
Oak Ridge National Laboratory*

ABSTRACT

Measuring the diffusivity of a gas in the unsaturated zones has a direct application to soil-gas surveys and to the prediction of contaminant movement via vapor phase transport. This paper proposes an in situ technique to measure the diffusivity of selected gases. The method involves an uncased borehole in which an interval is isolated using pneumatic packers. A gas is injected into the interval and allowed to diffuse into the surrounding rock. Changes in gas concentration in the borehole are measured by a downhole nondestructive method. The equations for describing diffusion out of a borehole are analogous to those for heat flow theory. The diffusion equation with the initial value and boundary conditions appropriate for this problem are solved. The resulting mathematical description of diffusion and the design for the downhole instrument are presented in this paper.

INTRODUCTION

Attention has recently been focused on the role of the unsaturated zone in the storage and transport of hazardous waste. At sites where hazardous waste is used, stored, or disposed of, it is common to find unsaturated zone monitoring as part of an early warning system to detect groundwater contamination. Subsequently, soil-gas surveys are being used to define the extent of a groundwater plume at sites where groundwater contamination has already occurred.

Vapor transport is an important mechanism for the transport of contaminants in the unsaturated zone. Quantification of vapor transport rates, however, is still limited. By measuring vapor transport, it is possible to predict the rate of movement of contaminants in the unsaturated zone and select the proper sampling depths and locations for soil-gas surveys.

Under isothermal and isobaric conditions gaseous diffusion is expected to be the major mechanism for vapor transport. This is because vapor-phase diffusion coefficients greatly exceed those for the aqueous phase. Organic vapors in the gaseous headspace of unsaturated aquifers are a significant aspect of volatile pollutant transport (5).

Several methods are available to measure the diffusion coefficient. Stallman (8) relates the diffusion of a gas in air to a porous media using an empirical coefficient related to tortuosity and the air-filled porosity. Laboratory measurements of diffusion coefficients of oxygen in porous media are discussed in papers by Taylor (9), and Shearer and others (7). In papers by Raney (6) and Lai and others (3), measuring oxygen diffusion in a porous media is extended to in situ field sites. Raney (6) describes a diffusion chamber which consists of a probe inserted into the soil to a depth of 12 inches. A chamber on the probe is filled with nitrogen, a small port is manually opened, and diffusion of oxygen from the soil into the chamber allowed to take place. At 10-minute intervals a valve is closed and the concentration of oxygen in the chamber is measured. Determination of the diffusion coefficient for flow into a spherical boundary is described by Crank (2).

Lai and others (3) describe a field method in which needles are inserted into the soil and oxygen is injected. The change in oxygen concentration is determined by gas chromotography through the same needle after increasing periods of time. The resulting spherical boundary value problem is also solved by Crank (2).

This paper presents a method to measure the diffusion coefficient of selected organic gases in an uncased borehole. Unlike earlier methods which remove a portion of the gas to analyze the concentration, this

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[1] Environmental Sciences Division
[2] Health and Safety Research Division
* Operated by Martin Marietta Energy Systems, Inc. under DOE contract No. DE-AC05-84OR21400.

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method uses a non-destructive technique to measure the in situ concentration of selected gases. Heat flow equations presented by Carslaw and Jaeger (1) are adapted to describe the boundary value problem of gaseous diffusion from a cylinder of radius, a, at an initial concentration C_0 into the surrounding porous media initially at zero concentration.

GOVERNING EQUATION

The mathematical representation of the diffusion of a gas through a porous medium is analogous to the mathematical representation of the flow of heat by conduction through a solid. Both diffusion and heat flow are described by the same differential equation. When no sources or sinks are present, the equation describing transport is,

$$\beta \nabla^2 F(x,y,z;t) = \frac{\partial F(x,y,z;t)}{\partial t} \qquad (1)$$

where $F(x,y,z,t) =$

$$\left[\begin{array}{l}\text{temperature, in the case of heat flow} \\ \text{concentration, in the case of diffusion}\end{array}\right],$$

expressed as a function of position and time,

and, β = a proportionality constant characteristic of the medium.

For heat flow, $\beta = \kappa$ (the thermal diffusivity of the medium).

And for vapor diffusion, $\beta = D$ (the effective diffusivity of the gas in the porous medium when the medium is considered macroscopically homogeneous).

It is assumed in this paper that β is constant and is independent of the function F.

Equation (1), has been solved for a wider variety of initial value and boundary conditions in the context of heat flow than for diffusion. For our application, solution for heat flow which is analogous to the diffusion problem is discussed in Carslaw and Jaeger (1).

For the infinite cylinder of radius a, consider the region r > a initially at zero temperature. At r = a, the region is in contact with a perfect conductor of specific heat c_s and mass density ρ_s, initially at temperature V_0. The specific heat and mass density of the medium, r > a, are c_m and ρ_m respectively. There is no contact resistance at r = a.

The temperature V(t), in the region r < a is given as

$$V = \frac{4\alpha V_0}{\pi^2}\int_0^\infty e^{-\kappa t u^2/a^2}\frac{du}{u\Delta(u)}. \qquad (2)$$

where V = the temperature in the cylinder as a function of time t, and κ = the thermal conductivity of the medium outside the cylinder.

$\alpha = \dfrac{2c_m\rho_m}{c_s\rho_s}$, a parameter which is twice the ratio of the heat capacities of an equivalent volume of the medium to that of the cylinder.

and,

$$\Delta(u) = \left[uJ_0(u) - \alpha J_1(u)\right]^2 + \left[uY_0(u) - \alpha Y_1(u)\right]^2 \qquad (3)$$

where $J_n(u)$ and $Y_n(n)$ are the ordinary Bessel Functions.

The solution of the diffusion equation with appropriate initial values and boundary conditions for the case presented in this paper has a similar form and is given as,

$$C = \frac{4\alpha C_0}{\pi^2}\int_0^\infty e^{-Dtu^2/a^2}\frac{du}{u\Delta(u)}, \qquad (4)$$

where C = the concentration in the cylinder as a function of time, D = the effective diffusivity of a selected gas in the porous media, a = the radius of the borehole, C_0 is the initial concentration in the borehole, $\Delta(u)$ is given in Eq. (4), and, α = is a parameter which is equal to twice the porosity of the media.

The diffusivity of a selected gas in the porous media, D, is a function of the gaseous diffusivity in free air, the tortuosity of the media, and any transient storage capacity of the media.

To calculate the diffusivity from test data, relative concentration values, (C/C_o), of gas in the borehole are plotted as a function of time on a semi-logarithmic scale. Curve matching techniques are then used to match the test data to the type of curves presented in Figure 1.

All practical precautions should be taken to ensure that the experimental apparatus designed to apply this theory to site conditions upholds the initial assumptions as closely as possible.

These assumptions are:

- An infinite, isotropic, macroscopically homogeneous medium.
- The diffusivity of the medium is a constant independent of concentration and position.
- The appropriate initial concentrations.
- Diffusion of particles takes place only through the voids in the medium, r > a. The solids in the region r > a are impermeable to diffusion.
- The only influence on particle transport is from the concentration gradient. Air movement and pressure gradients are either absent or negligible.

FIELD EQUIPMENT

It is apparent that borehole diffusion can be described mathematically and that the measurement of the parameters used in this description would be useful for modeling the transport of volatile contaminants in the vadose zone. Unfortunately, such measurements are not presently made in the field because potentially useful analytical techniques would cause too much disturbance to the system. Ideally, the measurement should be made in a packed-off section of a borehole as shown in Figure 2. Most commonly used analytical methods require pulling a vacuum to collect the sample. Thus, even if the amount of sample removed or recirculated in the borehole is small, the diffusion measurement will be affected. Commonly available field instruments such as HNUs, TIPs or non-dispersive infra red detectors cannot be used without making some correction for the effect of the measurement process on the measurement itself.

There are, however, some possible alternatives. One promising technique is the use of fiber optic optrodes. These devices employ a chemical substance at their tip which is sensitive to the contaminant of interest. This substance undergoes a chemical change that can be related to the concentration of the contaminant. Unfortunately, the development of such a tool is in its infancy and the device is not easily used for chemicals such as trichloroethene - a prime candidate for these measurements.

Recently, however, Oak Ridge National Laboratory has developed and licensed a device called an I-GAS chip (4). This device consists of a chemical "goop" sensitive to a particular contaminant. The heat conducting properties of the "goop" are affected by the presence of the contaminant. The change in thermal conductivity is directly proportional to changes in contaminant concentration. This system, in theory, is ideal for performing borehole diffusion measurements. The technique is non-destructive, it pulls no vacuum, nor is air circulated in any way. Only a small amount of heat is applied to the chip to make the measurement. We hope to report actual in-situ borehole diffusion measurements within a short time. We believe that these measurements will greatly aid the development of modeling capabilities for volatile contaminants in the vadose zone.

CONCLUSIONS

The diffusion coefficient is important in predicting isothermal/isobaric transport of organic vapors in the unsaturated zone. An in-situ technique is described which directly measures the diffusion coefficient of selected organic gases. This technique has direct implication for predicting vapor transport in the unsaturated zone and assisting in the design of soil-gas surveys. Future work should incorporate skin affects, the dependence of the diffusivity on gas concentration, the effects of soil water content on the transport of vapor, and the influence of different densities on gas movement in the borehole. In addition, the parameters influencing the effective diffusion coefficient should be mathematically stated. By independently measuring these parameters, selected unknowns can be evaluated based on effective diffusion measurements.

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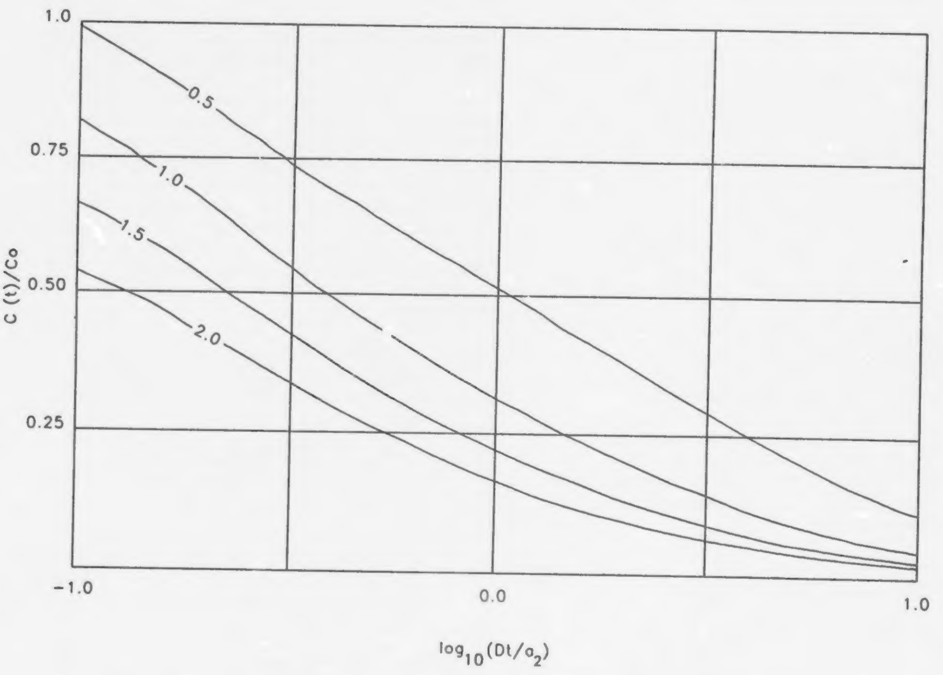
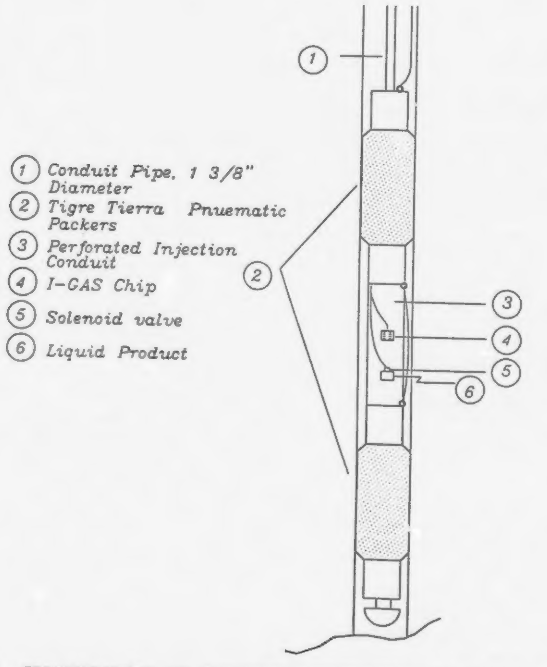


FIGURE 1 CONCENTRATION IN A CYLINDER OF A PERFECT CONDUCTOR, INITIALLY AT A CONCENTRATION C_o IN AN INFINITE MEDIUM INITIALLY AT ZERO CONCENTRATION. PLOTS ARE SHOWN FOR VARIOUS VALUES OF THE PARAMETER α .


① Conduit Pipe, 1 3/8" Diameter
② Tigre Tierra Pnuematic Packers
③ Perforated Injection Conduit
④ I-GAS Chip
⑤ Solenoid valve
⑥ Liquid Product
①
②
③
④
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⑥

FIGURE 2 ILLUSTRATION OF EQUIPMENT CONFIGURATION FOR IN-SITU BOREHOLE DIFFUSION MEASUREMENTS

DISCUSSION

JOHN EVANS: Can you expand on your argument that sampling points some distance from the borehole destroys the soil properties in some way. There are large volumes of soil in between, which is the main diffusivity medium, and conversely, if that's true, you've also disrupted the soil with the boreholes.

TOM CRONK: Regarding installing sensors in the soil and disrupting the soil properties, you mentioned that a large distance of soil would exist between the measurement sensors. That would, in effect, give you a realistic interpretation of diffusivity. That would be true, but you would have to introduce enough gas to diffuse through those large volumes you are talking about. In effect, that wouldn't be a good policy, we feel, because we would be introducing quite a bit of gas into the soil for a measurement.

Also, if the distance between the measuring devices was indeed large, the time factor required for the gas to diffuse through that distance would tend to make the measurements rather long, maybe weeks.

JOHN EVANS: You have disrupted the column by a fairly large diameter hole. How representative are the walls of the borehole, for example, relative to the undisturbed soil?

Also, what gas are you using?

TOM CRONK: We're going to test a device with toluene or benzene. Your point is well taken regarding the borehole. Those are questions that need to be addressed with further research with this device.

The rate at which soil passes from the borehole into the soil medium will be affected by the borehole. Perhaps there will be other effects and phenomena. We will need to make corrections, if we find that the error is substantial. Much will depend on the different types of soil we are using.

TOM SPITTLER: One of the problems I think you're going to encounter is the rate and the amount at which soil will adsorb, or absorb – I'm not sure which process – chemicals like benzene and toluene. How are you going to distinguish diffusion through the soil from adsorption to the soil?

TOM CRONK: That point has also been considered, and we're going to see how much error is introduced through actual measurements with our device.

Hopefully, it will be a small effect, maybe even short term, but we can test by taking measurements first in fresh soil, where the gaseous concentration was zero. Then, after the soil has been saturated, or has adsorbed as much as it can, we'll repeat the measurement, and see what different values we get.

TOM SPITTLER: I think you're going to find it's a fairly substantial factor for things like the aromatic hydrocarbons. You might have to put in a casing if these boreholes are not stable. Could your theory be modified to include a screen or casing, so that you would have a two-layer diffusivity equation?

TOM CRONK: Yes. The modification would take place in the porosity constant, and in effect, would physically change the porosity of the soil at the boundary, where the diffusion takes place. As long as we knew the grid spacing of the casing, I think we could incorporate that easily.

JOHN EVANS: There is a lot of literature on bacterial effects wiping out aromatics in particular. Isn't this a problem over short distances? I have seen numbers that say you have to be within a couple of feet of the water table to see any soil gas profile at all for those species.

TOM CRONK: That could be a problem, and we do need to address that with further research.

JOHN EVANS: Maybe you would be better off using something other than benzene and toluene.

RICHARD GLANZMAN: How are you differentiating transmissivity due to a pressure differential from the diffusivity?

TOM CRONK: We're assuming that there are no pressure gradients in the soil. Your question refers to how we intend to first establish the initial concentration in the borehole, without causing a pressure gradient.

The first technique utilizes a vial of highly volatile liquid, opened via a solenoid valve, followed by volatilization in the borehole. We feel that the pressure gradient introduced from this method will be negligible.

The second method we are thinking about is to inject the gas from a cylinder and vent the borehole at the same time, in effect holding the pressure constant. The borehole is full when we get the same concentration out the vent. Both are then shut at the same time.

PHILIP DURGIN: That was an excellent problem to work on. We're dealing with that kind of question with underground storage tanks. We're asking, are the backfilled materials sufficiently porous and permeable to allow gases to diffuse, so you can have vapor monitoring? It's a good tool to be used in the future, if it works out.

A Field Method for Determination of Volatile Organics in Soil Samples

Thomas M. Spittler and Mary Jane Cuzzupe
USEPA Regional Laboratory
60 Westview St.
Lexington, MA 02173

J. Tyler Griffith
Goldberg, Zoino & Assoc., Inc.
27 Naek Road
Vernon, CT 06066

With the growing concern for leakage from underground storage tanks and the realization that such leaks can be a serious threat to water supplies, there has arisen a need for better and more rapid methods to assess such problems. The use of soil gas analysis coupled with various field monitors, notably portable gas chromatographs, has given investigators a powerful tool to assist in locating and pinpointing leaks. Once a leaking tank has been identified, there is the question of how much contamination is residual in the surrounding soil. Several attempts have been made to develop a method for determining soil contamination by volatile solvents. At the present time, none is truly satisfactory as a field method, though several show some promise.

Following a suggestion from our lab, Pojasek and Scott developed a surrogate screening method in 1981 (1). They took an aliquot from collected cores and placed it in a tared VOA vial, added 10 ul of 1% $HgCl_2$ to retard biodegradation and filled with organic free water from a buret. The volume of water was recorded for dilution calculations. Samples were stored at 4°C till analyzed. Before analysis, the sample was homogenized ultrasonically and ten ml of aqueous solution was withdrawn into a 40 ml VOA vial. After 30 minutes for equilibration, headspace analysis was performed.

In 1983 we suggested a rapid screening procedure (2) using a similar but more field suitable technique. Pretared vials were spiked with 20 ul of 2% $HgCl_2$ and filled with 20 ml of organic free water. Into these labeled bottles approximately 10 g of soil was placed while collecting samples in the field. Where immediate results are needed, the sample can be shaken for a few minutes and headspace analysis performed on the spot. After postweighing to determine the weight of soil, calculations can be made on concentration in the original soil.

Based on some results from the Ada, OK Laboratory, shown the author by Dr. John Wilson (3), the technique was modified so that only about one gram of soil was used in 30 ml of water. This method was discussed with Tyler Griffith who tested the technique using typical aromatics from hydrocarbon fuels (Benzene, Toluene, Ethylbenzene and Xylenes). This investigation was conducted as Mr. Griffith's MS thesis at the University of Connecticut (4).

At about the same time, John Fitzgerald was developing a field screening method for gasoline-contaminated media for his MS thesis at the University of Lowell (5). Most of this work was done using a portable total organic analyser (Hnu PI-101) and measuring headspace vapor above soils. He found fair correlation between samples and discovered that the larger the sampling jar, the better the results. This was owing to the rather high flow rate of the Hnu sampling pump, and the consequent dilution of headspace in small jars.

EPA's Superfund program has published a method for analysis of volatiles in soil (SW846, 5030). This method involves collection of the sample in a VOA vial and return to the laboratory where an aliquot is extracted with methanol. The methanol extract is then diluted in water and submitted for standard purge and trap GC/MS analysis. We found that this technique resulted in severe loss of volatiles with time. For example, TCE levels dropped 80% after only 1 day holding time and were 90% lower after 14 day holding at 4°C.

All of the above methods have strengths and weaknesses. No in-depth study of the methods has been conducted to date. However, it is possible to point out the problems and some possible solutions based on one or more of the techniques described. The presentation will discuss in greater detail the method investigated by Griffith and show some data, on the problems with

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5030. The limitations of Fitzgerald's method are obvious because there is no possiblity of determining the exact composition of a volatile sample using a total analyser like the Hnu PID monitor. Pojasek and Scott's technique has some obvious advantages when a large number of samples must be screened without the advantage of Purge and Trap GC/MS equipment.

It is clear from this discussion that there is still room for method development in this important field. Rapid and accurate analysis of field samples is frequently needed to determine the extent of contamination in order to make decisions on removal, air stripping or vacuum extraction cleanup. It is especially necessary to know when a site is clean enough to stop remediation and begin site closure. Unfortunately, many regulations have already been put in place to determine "how clean is clean", but few, if any, can specify with confidence the methodology by which field samplers, chemists and site managers are to make that determination.

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DISCUSSION

JOHN EVANS: In some cases, sensitivity is a problem, if you insist on using GC/MS rather than gas chromatography.

THOMAS SPITTLER: I don't insist on using GC/MS. A GC/MS is nothing but an expensive gas chromatograph that does a very nice job if you have to get absolute, incontrovertible identification. But it hasn't got sensitivity. Work is now being done to get it down to the part per billion level, or below, where we can get down to the part per trillion level in the field, with an instrument that costs about five percent as much.

JOHN EVANS: How about other ways of improving the exchange, such as adding methanol to the water? What is your opinion on direct purge-and-trap methods for soil, without any addition of solvents, provided you have a mobile laboratory available.

THOMAS SPITTLER: That's one of the SW846 options, that you can take the sample, add it to water, and purge it directly. The second suggestion is excellent – maybe a small methanol concentration in the water solution to improve the speed with which you do the extraction.

Now for the aromatics, let me caution that these are not real-world samples. These are spikes, and as any good chemist will tell you, a spike is like an expressway ramp: easy on, easy off. But when you take a sample that's been in the real world for a year, or a decade, or a half a century, it's a totally different matter to get it out of the soil quantitatively.

This is a very important point. Do you have to get it out quantitatively? If rainwater flowing through it for 30 years can't wash it out of the soil, why should we dig up that soil and extract it with methanol? It isn't going to go anyplace.

DON FLORY: Have you compared the values that you would get by the purge-and-trap technique, which is what's called for in SW846 and the CLP for low levels?

THOMAS SPITTLER: Yes Mr. Griffith did use the standard method. He had it done at the State Laboratory in Connecticut, and they compared pretty favorably with his answers, until the samples were held more than three or four days. And then the state lab results were very, very low, compared to what he had in those original soil samples. There was a volatile loss.

TOM STOLZENBERG: To address the question about direct purge and trap, we had a soil contaminated with tetrachloroethylene. We took splits of that sample, analyzed it by direct purge and trap, in water, and also by TCLP. We got seven times more tetrachloroethylene by the TCLP leaching method than we did get by direct purge and trap. In the TCLP leaching method, the soil is subjected to a much longer period of extraction, so to speak, which we reasoned had a lot to do with the rate at which the perchloroethylene is emanating from the soil particle itself.

This leads to the question, did you spike those lab soil samples then look at grain size distributions and the effects?

THOMAS SPITTLER: The ones with the aromatic hydrocarbons were spiked. The samples with the TCE were real-world samples. That was the first set of work that I showed you.

TOM STOLZENBERG: We feel that there are a big differences in the rates of extraction, depending on whether the soil has been directly contacted with the PCE itself, or has been exposed via vapor. We feel that it takes a lot more to extract the perchloroethylene out of soil that has been in direct contact with the pure product.

THOMAS SPITTLER: You're absolutely right. That points out the need for some good, sound research on chlorinated solvents. Here's a very simple experiment you can try, if you get back to your lab, and you have a GC. Take a drop of trichloroethylene, put it into a bowl or vial full of water, and then take another bottle and put the same size drop of benzene or toluene or any aromatic hydrocarbon, and watch them.

If you do the trichloroethylene first, and then go to the benzene, you'll be able to watch them both. If you do the benzene first, and then the trichloroethylene, the benzene will be dissolved before you can get back to look at it.

The trichloroethylene will sit there for about three or four hours. A little drop, far below the solubility limit of any of the chlorinated solvents, goes into solution. You can shake it up, and you may think you put it into solution, but what you've done is created a suspension of very tiny microdrops. They will be in true solution by tomorrow morning, but it takes a long time.

The kinetics of solubility pose very interesting problems with chlorinated solvents. Therefore, when you're trying to extract them from the soil, you're relying on those kineticss which complicate the issue.

We recognize the problem. What we have to do now is devise a method for increasing the rate at which this happens. One of the suggestions I heard yesterday at the meeting was to take a little sonicater with you, with a very low power requirement. You can plug it into a small invertor or a small power supply. Sonicate the sample, when you're looking at the chlorinated solvents in soil. I have a feeling it would work.

BERNIE BERNARD: In the late '60s and '70s, almost identical work was being done by a group of people in geochemical prospecting for oil. In those studies, holes were poked in sediments offshore, and soil gases were done onshore. The same kind of data found here were generated with a couple of minor differences.

First, the volatile gases would partition into the gas phase on equilibrium, in relation to their solubility coefficient, so that their actual concentrations as measured from head space would have to be normalized by the partition coefficient, namely for benzene. For instance, the gases would partition to the extent of only 60% to 70% in the headspace, under the conditions you gave.

So the answer you obtained would have to be divided by say 0.6, or 0.65 to get a true answer. If you strip the headspace off and reequilibrate, you get another 60%, etc.

THOMAS SPITTLER: The headspace principle is to prepare a standard with the known concentration in the aqueous phase, and then equilibrate the same way you do the unknown. Then you use the headspace measurement as a surrogate for the liquid phase concentration. This is a very accurate and precise quantitative analysis of dissolved solvents, and we've got data to show that this holds down into the part per billion range for aqueous solvents.

But you've got to take into account the in-rock constant if you're going to use the concentration in the headspace as the final measure. It's just a surrogate, and you compare it with the concentration of known standards to calculate what's in the aqueous phase.

BERNIE BERNARD: We found a particle size effect, that shales and very fine clays caused the equilibrium not to push toward the headspace nearly as quickly as sandy material. So in the real world, there may be some effect of particle size.

THOMAS SPITTLER: I'm sure there is that effect, in that the evidence of the effect is here. But this is not real-world sampling. This is thesis, and it's got to be tested in the laboratory, where we've got some control.

BERNIE BERNARD: You were commenting on the ultimate sensitivity being in the mid parts per trillion. Our experience with purge and trap is that we are trying to achieve several parts per billion level with a five-cc sample, and you're talking about achieving an order or two orders of magnitude lower than that, with a 200 mL sample.

THOMAS SPITTLER: Three orders of magnitude.

BERNIE BERNARD: With the same types of detection?

THOMAS SPITTLER: No, this is the photoionization detector, not a mass spectrometer.

BERNIE BERNARD: I'm talking about photoionization detection in laboratories.

THOMAS SPITTLER: You're not talking about Photovac PID, because it's about two orders of magnitude more sensitive than the conventional PID's that have been on GC's for years.

BERNIE BERNARD: No, I'm not. I guess I'm referring to the fact that most labs around the country are having trouble achieving the method detection limits for method 502.2, which are on the order of 0.01 to 0.05 ppb. They are having trouble with that. Yet, you're saying you can easily achieve sensitivities using a hundred-fold less sample size with this particular detection.

THOMAS SPITTLER: Ask a few of the people here with those Photovacs who are GC practitioners. It's unbelievable what you can do with a good trained chemist.

UNIDENTIFIED PARTICIPANT: Have you tried thermal desorption?

THOMAS SPITTLER: Yes, it can be done, but it's still going to give you just a relative measure, and what we're looking for now is some way to get a quantitative measurement, especially when you're talking about a multi-million dollar decision about whether to dig it up, vacuum extract it, turn it into concrete, or any of the other things being done at some Superfund sites, before we know what the real problems is. That's a serious issue, and a lot of money goes down the drain on very poor, ill planned technology.

SOIL-GAS SAMPLING AT A SITE WITH DEEP CONTAMINATION BY FUELS

H. B. Kerfoot, S. R. Schroedl
Special Projects Office
Lockheed Engineering and Sciences
Company, Las Vegas, Nevada

J.J. D'Lugosz
Advanced Monitoring Division
U.S. EPA Environmental Monitoring
Systems Laboratory
Las Vegas, Nevada

ABSTRACT

Soil-gas sampling and analysis is a technology finding widespread acceptance as a preliminary screening method for delineation of subsurface contamination. In an arid climate, a complex of 4-21' outside diameter underground storage tanks were investigated using soil-gas sampling, EPA method laboratory analysis of soil samples, and GC/MS analysis of groundwater samples. Because of the relatively thick vadose zone (85' - 90' to the water table) and low volatility of the fuel contaminants, there was a significant chance that the technology would not detect the contamination. However, the results of the soil-gas survey reflect steep hydrocarbon gradients near the tanks and more gradual gradients some distance from the tanks. These results, as paralleled by the soil analysis and ground water analysis, indicate shallow soil contamination near the tanks that leans to deeper ground water contamination at a distance from the tanks.

INTRODUCTION

Soil-gas surveying is a technology finding widespread acceptance as a preliminary screening method for delineating of subsurface contamination (1) and underground storage tank leakage (2). The technology originated in the 1920's for use in petroleum exploration (3). More recently, soil-gas sampling and analysis has been used for investigation of vadose zone properties (4).

Environmental application of the technology was first done in Europe and more sophisticated sampling and analysis methods were later applied in studies of landfill gases and detection and delineation of ground-water contamination by volatile organic compounds (VOCs). The U.S. Environmental Protection Agency has funded evaluations of techniques (1, 5, 6, 7) and EPA (8) and private (9, 10) workers have applied forms of the technology. Other studies have applied the technology to determine vadose-zone transport properties (11). Bulk grab sampling (1), sorbent grab-sampling (10), and passive-sampling (6) techniques have successfully been used for measurement of VOCs in soil gases. On-site analysis and remote analysis of samples have both been performed, and a wide variety of instrumentation, including detector tubes, portable organic vapor detectors, and gas chromatography with mass spectrometry (GC/MS) have been used.

Much progress has been made in the understanding of the factors that determine soil-gas concentrations in the area of the subsurface contamination . Chemical and physical properties of the contaminants, physical transport of VOCs from the contamination to the sampling location, and subsurface fate of the target VOCs during transport influence soil-gas VOC concentrations at a given sampling location (12).

The physical properties of the contaminant that most affect soil-gas concentrations are vapor pressure, diffusion coefficient, and Henry's Law constant. The vapor pressure and Henry's Law constant are important for estimating the magnitude of the vapor concentration in contact with contamination from soil or ground water contamination, respectively. Lower soil-gas concentrations in contact with contamination can result in lower shallow soil-gas concentrations thereby reducing the sensitivity of the technology. Lower volatility fuels,

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such as diesel fuel, can be a problem for soil-gas surveying technology for this reason (13). The diffusion coefficient of the compound directly influences the vadose-zone transport rate (see below) and is typically acceptable for vapor pressures and Henry's Law constants. The thicker the vadose zone is at a site, the more important this physical property is, because of the increased influence of transport in shallow soil-gas VOC concentrations.

Because diffusion is the primary mechanism for gas transport in soils (14, 15), vadose zone properties that affect diffusion are a major factor in determining vadose-zone transport rates. Modified forms of Fick's Law have been derived to describe diffusion in porous media, and all show that diffusion is negligible when the connected air-filled porosity of the medium falls below approximately 10 percent. This means that continuous layers of clay and perched water bodies can serve as barriers to diffusive transport. As in all mass transport, VOC concentrations downstream of the slowest step of the process will be depressed. For that reason, such situations can create a situation where the technology is not applicable.

In this paper we describe a soil-gas survey for jet fuel with monitoring-well and soil-boring confirmation of the results at a site with 85 to 90 feet to the water table. The contamination at the site is due to leaky waste-fuel tanks that contained jet fuels that are dominated by low-volatility hydrocarbons. Because of the relatively thick vadose zone and low volatility of the fuel contaminants, there was a significant chance that the technology would not detect the contamination. We discuss our findings and what level of contamination the technology was able to detect.

SITE DESCRIPTION

The site used in this study contains four 21-foot diameter concrete underground storage tanks (numbers 22, 23, 24, and 25) arranged linearly and separated by 3 feet. Between 1946 and 1974, the site had been operated as a heating oil storage and pumping station and since 1974 as a solid waste and waste fuel storage area. The tanks, as well as waste drums and crates are enclosed within a 100-foot-wide by 200-foot-long, 5-foot-high chain-link fence. Near the fenced area, three monitoring wells have been drilled to the water table (85 - 90 feet). Figure 1 provides a detailed map of the site indicating concrete tanks and monitoring wells and Table 1 provides a description of soil types encountered in the soil borings.

METHOD

The data compared in this study was obtained using three different techniques, including soil-gas grab sampling with on-site analysis, laboratory analysis of soil samples using EPA approved methods, and review of monitoring well data. Each technique is described in more detail below.

Soil-Gas Sampling and Analysis

Soil-gas measurements consisted of 66 sampling points in and around the compound (see Figure 2), determined as the survey developed. Soil-gas samples were taken from a depth of 7 feet using 0.25-inch OD/0.125-inch ID stainless steel probes approximately 7.5 feet long. Probe emplacement involved hammering a 1-inch driving bar into the ground to a depth of 7 feet, removing the bar, inserting the probe in the void, and backfilling with native fine-grained material. With the probe in place, a manifold with septum was attached as was a 100-cc MSA Samplair vacuum pump. Samples were taken through the septum using a clean 1-cc Hamilton Gastight syringe after 200 cc (two pump volumes) was purged through the probe.

The sample was taken immediately to the field trailer for analysis. Analysis was by either Shimadzu GC-3 gas chromatography/flame ionization detector (GC/FID) for total hydrocarbons or AID Model 511 has chromatography/electron capture detector (GC/ECD) for the chlorinated compounds 1,1,1-trichloroethane (TCA), trichloroethene (TCE), and tetrachloroethane (perchloroethylene or PCE). The Shimadzu was operated with a 6' x 1/8" SS column packed with 10% SP-100 chromosorb at a temperature of 65°C and a 200°C injector and detector temperature. The AID operated with 6' x 1/8" SS 0.1% AT-1000 Graphpac column. Column and detector temperatures were both 105°C and the injector temperature was 112°C.

Soils

Soil boring and sampling were done at 7 locations in and around the area of investigation (locations A through G in Figure 3). A conventional auger was used to drill each boring to a depth of 20 feet. The locations of these borings were chosen to investigate the areal extent of shallow (<20 feet) soil contamination at the site. Borings A - C were intended to confirm the indication, based on the soil-gas data, of shallow soil contamination near the tanks. Borings D, E, F, and G were intended to confirm the boundaries of shallow horizontal migration as indicated by the soil-gas results. Samples were taken at 5 feet, 10 feet, 15 feet, and 20 feet using a spit-spoon sampler containing 12 1-inch long brass sample rings. Each split-spoon sample was divided into four equal portions, one for soil identification and three for laboratory analysis. Each of the splits was wrapped in aluminum foil and duct tape to contain volatiles.

Monitoring Well Data

Monitoring wells were drilled by James M. Montgomery Engineers to a depth of 110 feet. The number of wells drilled was predetermined independent of any subsurface contamination data and well locations of one up-gradient and two down-gradient from a potential contamination source were chosen on the basis of past experience.

RESULTS AND DISCUSSION

Soil Gas

The data gathered during the soil-gas survey included the characterization samples as well as duplicate samples, serial samples, and temporal variability samples used for comparative analysis. Table 2 provides the temporal variability data as an example of the type of reproducibility encountered. The results of the comparative analyses between these types of samples indicated an order-of-magnitude delineation of soil-gas concentrations was a representative indication of soil and groundwater contamination by hydrocarbons. Figure 4 shows this order-of-magnitude interpretation as isoconcentrations of the soil-gas total hydrocarbon results. Further analysis of this interpretation shows horizontal concentration gradients close to the tanks are large, consistent with shallow soil contamination as the source of the VOC vapors. The lower gradient pattern of soil-gas total hydrocarbon contamination that extends generally to the east/east-northeast is in the general direction of the local ground-water gradient and is consistent with contamination located much deeper. There is also an indication of a small lobe of elevated soil-gas concentrations to the south of tanks 22 and 23, suggesting some southerly horizontal migration of fuels there.

Figures 5, 6, and 7 show chlorinated-hydrocarbon soil-gas isoconcentration contours for tetrachloroethene (PCE), 1,1,1-trichloroethane (TCA), and trichloroethene (TCE). Both the TCA and PCE spatial distributions are very similar to the total hydrocarbon spatial distributions. However, for TCE, the pattern of soil-gas concentrations is quite different, showing the major amount of detectable TCE concentrations near and south and east of tanks 22 and 23.

Soils

Tables 1 and 3 list the results of soil analyses for selected volatile organic compounds and total hydrocarbons. Analysis of these results show two distinct trends; i) contamination, when present in the 20 foot boreholes, is found only in the boreholes nearest the storage tanks (boreholes A, B, and C), and ii) the contamination profiles for the boreholes show both increasing and decreasing contamination with depth. These trends are consistent with the soil-gas trends in showing shallow near-tank soil contamination and deeper (beyond 20 feet) contamination away from the tanks. However, the added information of the contamination profile increasing with depth indicates the contamination is not merely surface spill oriented but also involves a source at some depth beyond 10 feet below the surface.

Monitoring Wells

Well log data taken from field notes show the water table to be at approximately 80 feet with an 8 foot non-aqueous petroleum layer (NAPL) on the water table in well 12. HNU readings were low (0.2 to 2.2) and non varying in wells 11 and 13 and increased without interruption in well 12 from 1.4 at the surface to 140 at 70 feet.

Table 4 shows the result of analyses of ground-water samples form wells 11, 12, and 13. GC/MS analysis of ground water from wells 11 and 13 indicates low to non-detect concentrations of VOCs. GC/MS analyses of the ground water and of the NAPL showed the presence of C-7 to C-12 compounds in the NAPL and benzene, ethylbenzene, toluene, and xylene in the water. Field GC/FID analysis of the ground water and NAPL indicates a strong component of pre-benzene hydrocarbons in both.

Characterization of Contamination at the Site

As stated earlier, the soil-gas sampling locations were chosen as the survey progressed. Although an objective of the sampling plan was to have less than 1 order of magnitude change of total hydrocarbon concentration between any adjacent pair of sampling locations, this was not feasible near the tanks because of the very high horizontal concentration gradients there. In contrast to the high total hydrocarbon horizontal concentration gradient near the tanks as seen in Figure 4, gradual soil-gas concentrations gradients can be seen to the east of tank 22 and to the south of tanks 22 and 23. Evaluation of the distance-dependence of Fick's Law as well as past soil-gas investigations (16) indicate that at sites having a significant depth to ground water, such as this site, shallow contamination (ca, 10% of the depth to ground water) produces a much higher soil-gas concentrations gradient than is seen from a ground-water VOC source characterized by gradual isopleth gradients.

Using the high vs. gradual isopleth gradient comparison, initial interpretation of the soil-gas data lead to the conclusion that the site contains shallow soil contamination near the tanks and a minimum ground water contamination plume indicated by the 100 mg/m^3 contour in Figure 4. Further site investigation of monitoring wells, soil borings, and transport theory supported this interpretation by 1) determining the presence of free product in well 12 which is within the 100 mg/m^3 contour and the absence of product in wells 11 and 13 which are outside of the 100 mg/m^3 contour; 2) an uninterrupted increasing HNU readings from 1.4 to 140 at 70 feet thereby indicating the groundwater as the only source of hydrocarbons; 3) the absence of soil contamination in certain boreholes to at least 10 feet as a result of the soil boring analyses indicating a subsurface source as well as surface spill contamination; and 4) providing a mechanism for horizontal migration of hydrocarbons regardless of the ground-water gradient through experiments in test chambers of hydrocarbons in contact with groundwater (17) thereby explaining the cross-gradient lobe to the south of tanks 22 and 23.

Soil-gas surveying for TCA, TCE, and PCE was done to investigate the possibility of surface spills of solvents within the site. The coincidence of the TCA, TCE, and PCE spatial distributions with at least part of the petroleum hydrocarbon distribution, the parallel tendency of increasing chlorinated hydrocarbon and hydrocarbon soil contamination with depth, and the low volatility/high immobility of chlorinated hydrocarbons indicating the inability to move on their own, leads to the possibility they were present as impurities in the fuel that leaked.

CONCLUSION

In this field study, several noteworthy results were obtained. It was shown that soil-gas hydrocarbon VOC concentrations can serve as an indicator of non-aqueous petroleum liquids on a deep (80 feet) water table. The fact that steep horizontal contamination gradients are indicative of shallow soil concentration above a deep aquifer was also borne out by results.

In addition, the data indicate that temporal variability of soil-gas concentrations over a period of 24 days did not create significant bias or data-comparability problems with soil-gas data at this site. As with any field method, the data should be considered preliminary and requiring additional supporting data from additional monitoring wells and analyses of soil borings from more than 15 feet.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support and assistance of James M. Montgomery Engineers.

NOTICE: Although this research was funded in part by the U.S.EPA through Contract 68-03-3249 to Lockheed Engineering and Science Company, Incorporated, it has not undergone Agency review and does not necessarily reflect Agency policy.

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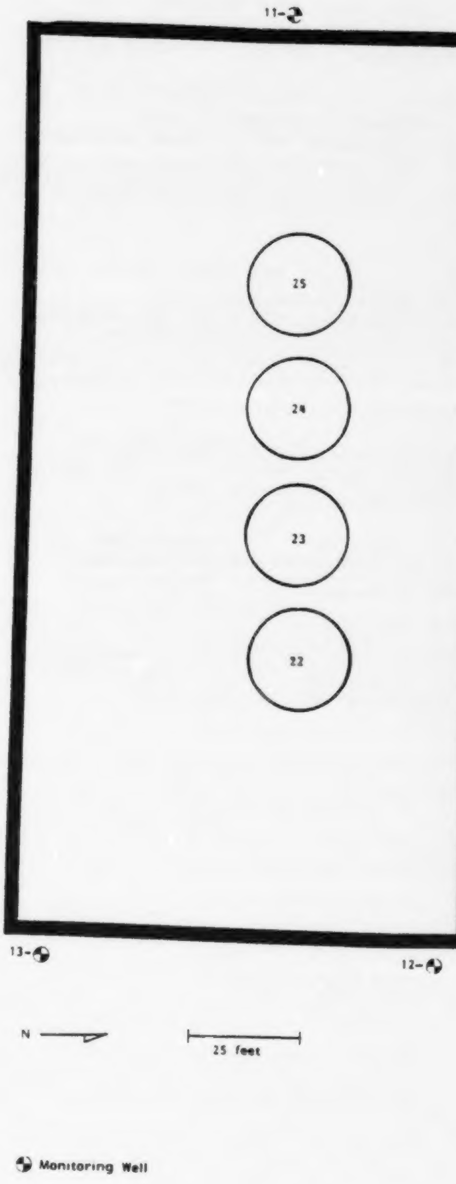
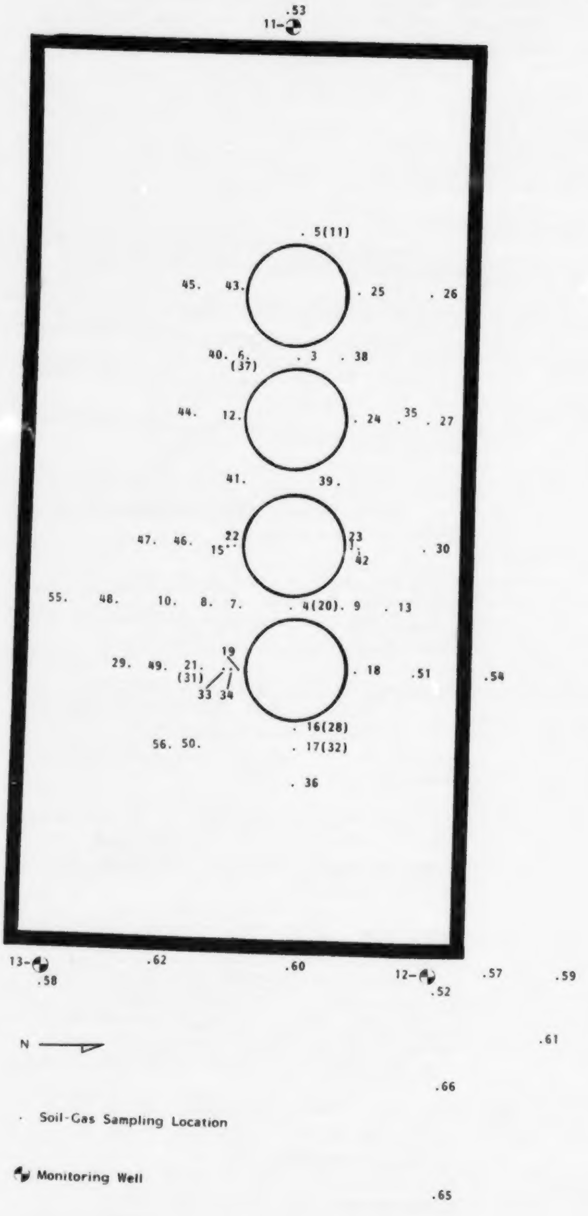

11-
25
24
23
22
13-
12-
N
25 feet
Monitoring Well

Figure 1. Site Map


.53
11-
. 5(11)
45.
43.
. 25
. 26
40.
6.
(37)
. 3
. 38
44.
12.
. 24
.35
. 27
41.
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47.
46.
22
15
23
1
42
. 30
55.
48.
10.
8.
7.
. 4(20).
9
. 13
19
29.
49.
21.
(31)
33
34
. 18
.51
.54
. 16(28)
. 17(32)
56.
50.
. 36
13-
.58
.62
.60
12-
.52
.57
.59
N
.61
.66
Soil-Gas Sampling Location
Monitoring Well
.65

Figure 2. Soil-Gas Sampling Locations

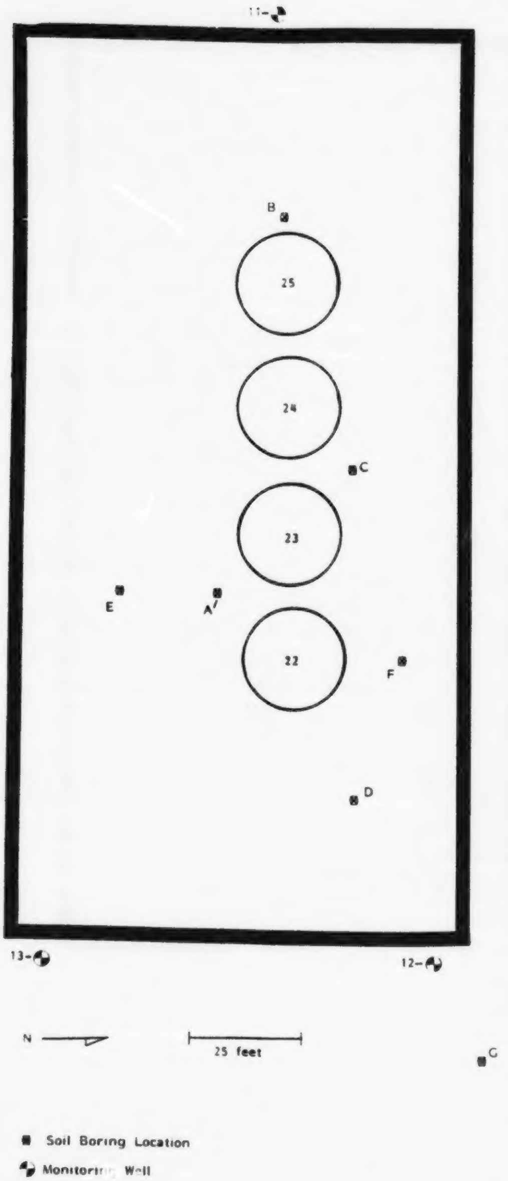

11
B
25
24
C
23
E
A
22
F
D
13
12
N
25 feet
G
Soil Boring Location
Monitoring Well

Figure 3. Site Map with Soil Boring Locations

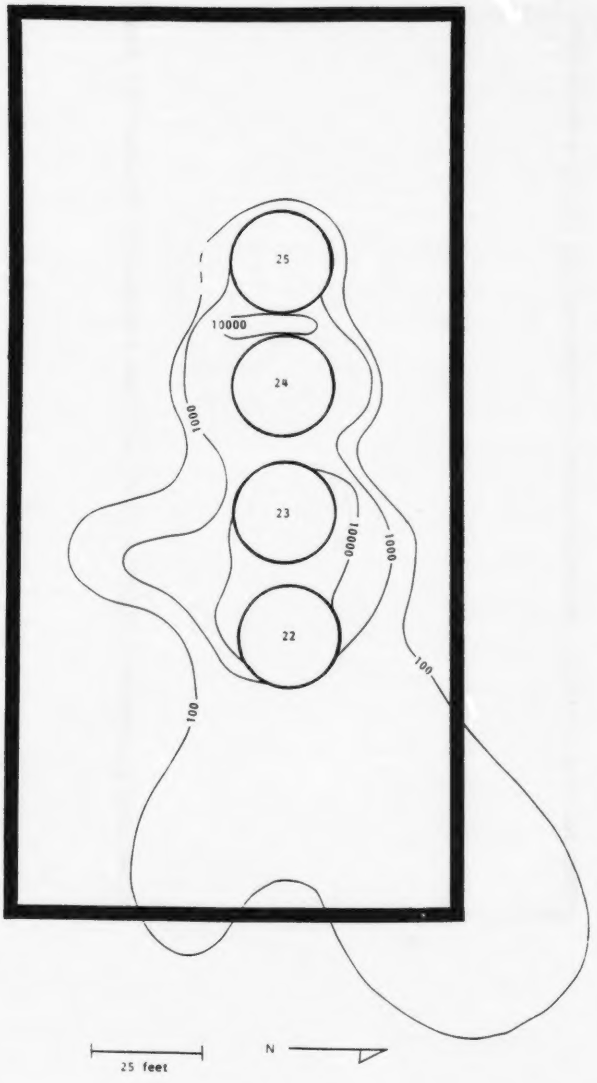

25
10000
24
1000
23
10000
1000
22
100
100
25 feet
N

Figure 4. Total Volatile Hydrocarbon Soil-Gas Concentrations (mg/m^3)

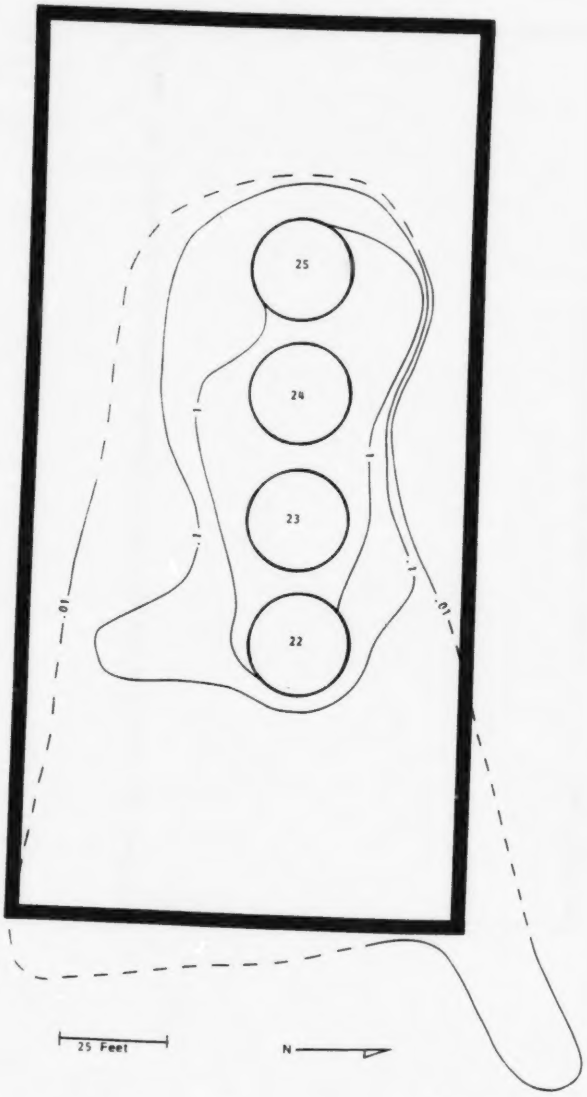

25
24
23
22
1
1
.01
1
.01
25 Feet
N

Figure 5. PCE Soil-Gas Concentrations (mg/m^3)

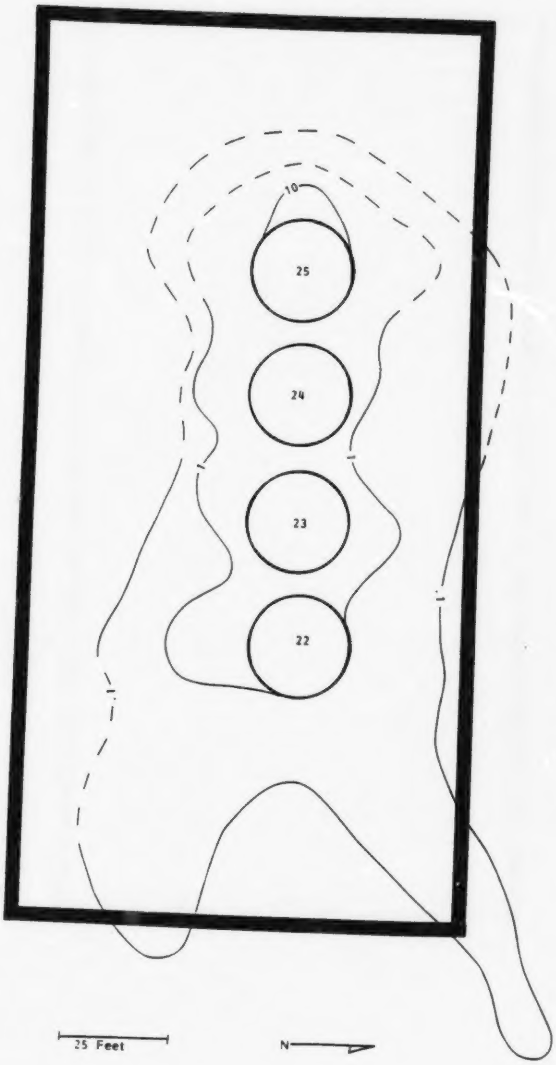
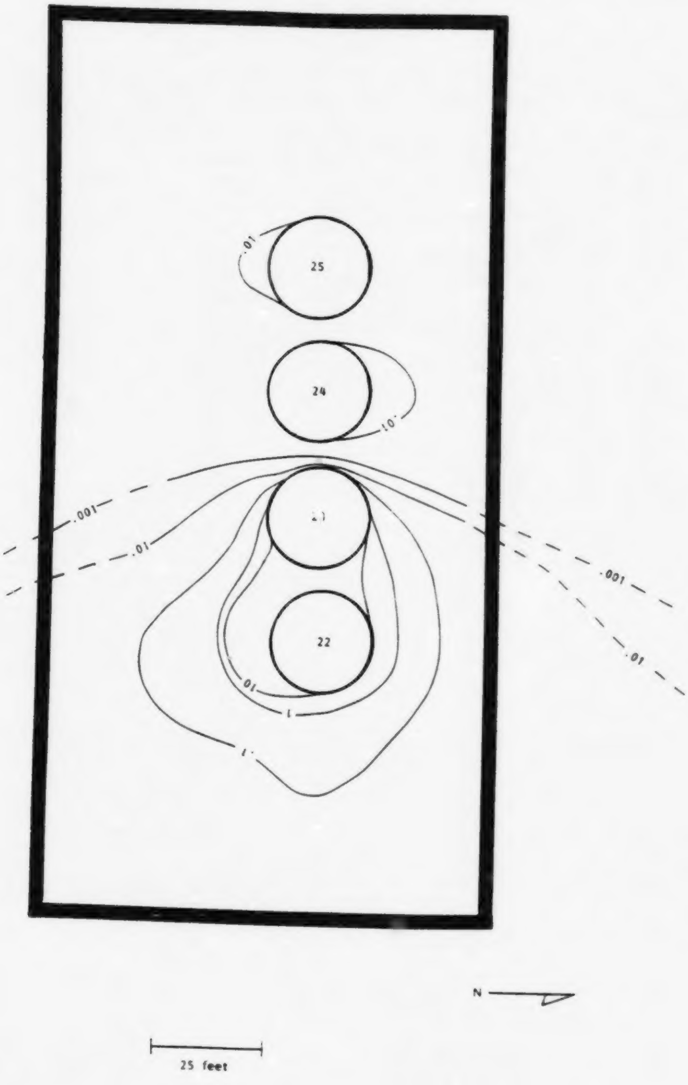

10
25
24
23
22
1
1
1
1
25 Feet
N

Figure 6. TCA Soil-Gas Concentrations (mg/m^3)



.01
25
24
.01
.001
.01
21
22
.01
.01
1
1
.001
.01
N
25 feet

Figure 7. TCE Soil-Gas Concentrations (mg/m^3)

Table 1. Selected Volatile Organic Compounds (EPA Method 8240) Concentrations (ug/kg)

Sample	Soil Type	Toluene	Ethyl-benzene	Total Xylenes	TCA	PCE
A10	CL w/gravel	160	<10	<10	<10	33
A15	CL	4600	7300	43000	<100	<110
A20	ML w/sand & gravel	400	240	5400	<100	<100
B10	CL w/sand	130	34	170	130	71
B15	SC-SM w/gravel	10	<10	63	<10	20
C5	ML w/gravel	<10	<10	26	<10	120
C15	CL	120	<10	13	62	23
D5	SC w/gravel	2	<2	<2	<2	<2
D10	CL w/gravel	<2	<2	<2	<2	<2
E5	SC w/gravel	<2	<2	<2	<2	<2
E15	CL w/gravel	<2	<2	<2	<2	<2
F5	CH	<2	<2	<2	<2	<2
F15	CL	<2	<2	<2	<2	<2
G5	CL	<2	<2	<2	<2	<2
G15	CH w/gravel	<2	<2	<2	<2	<2

Table 2. RESULTS OF TEMPORAL EFFECTS ON SAMPLING PROBES (Concentrations in ng/cc)

Probe Location	Date Sampled	Total Petr. Hydrocs	TCA	TCE	PCE
4	3/22/88	51,000	-	-	-
	4/15/88	80,000	-	-	-
16	4/14/88	63	0.58	3.13	0.1
	4/19/88	13	0.62	1.61	0.1
17	4/14/88	35	0.37	0.39	0.0
	4/21/88	40	0.26	0.12	0.0
21	4/15/88	50	1.30	0.67	0.1
	4/21/88	71	1.24	1.14	0.1

Table 3. Total Hydrocarbons in Soil Samples

Borehole	Depth	Soil Type	Headspace Conc (ng/cc)	Lab Conc* (ng/g)
A	5	CL	11.8	-
	10	CL w/gravel	-	-
	15	CL	19,500	270
	20	ML w/gravel	11,400	480
B	5	CL w/gravel	226	-
	10	CL w/sand	1317	-
	15	SC-SM w/gravel	17.3	-
	20	-	24.8	-
C	5	ML w/gravel	20.8	<100
	10	CL	123	<100
	15	CL	204	<100
	20	SC-SM w/gravel	15.1	<100
D	5	SC w/gravel	10.2	190
	10	CL w/gravel	24.4	<100
	15	CL	146	<100
	20	-	99.4	100
E	5	SC w/gravel	42.7	270
	10	SC-SM w/gravel	23.2	<100
	15	CL w/gravel	-	160
	20	ML	17.8	1000
F	5	CH	20.8	120
	10	CL w/gravel	<20	<100
	15	CL	20.8	<100
	20	CL	17.8	1000
G	5	CL	10.6	320
	10	CL w/gravel	8.4	170
	15	CH w/gravel	13.6	100
	20	CL-ML	32.1	100

* Lab analysis used EPA Method 418.2

Table 4. Ground Water and Non-Aqueous Petroleum Layer Analysis Data (values in mg/l)

Compound Tested	Well 11	Well 12	NAPL	Well 13
Benzene	0.3	6800	520	ND
Ethylbenzene	ND	440	820	ND
Toluene	ND	9100	4000	ND
m,p-Xylenes	ND	770	1200	ND
o-Xylene	ND	740	900	ND
Bromoform	0.3	ND	ND	ND
Chloroform	0.2	ND	ND	ND
Dichlorobromomethane	0.2	ND	ND	ND

SOIL GAS ANALYSES TO DELINEATE A PLUME OF VOLATILE ORGANIC COMPOUNDS FROM A HAZARDOUS WASTE SITE IN WILLIAMSON COUNTY, TENNESSEE

Roger W. Lee
U.S. Geological Survey
A-413 Federal Building
Nashville, TN 37203

Mario Fernandez
U.S. Geological Survey
4710 Eisenhower Blvd. Suite B-5
Tampa, FL 33634

ABSTRACT

Volatile organic compounds, such as toluene and chloroethylenes, are known to migrate from underground disposal sites by advection in ground-water flow and to volatilize into the unsaturated zone above the water table. The dynamic characteristics of these compounds permit their detection by proper sampling and analysis of soil gases in the unsaturated zone. The disposal site, where as much as 44,000 gallons of industrial wastes were buried in pits in 1978, consists primarily of disturbed clay-rich regolith overlying Ordovician carbonate rock. In sampling soil gases at the site, a hollow steel shaft, about 6 feet in length and 3/4 inch in diameter, fitted with a drill head was used to bore to various depths into the unsaturated zone. Soil gases were drawn through ports located behind the drill head into capillary tubing inside the shaft, through a septum-sealed port at the top of the shaft, and into a gas syringe. Where contaminants were repeatedly encountered, hollow soil probes made of copper tubing were thoroughly decontaminated and used to collect the soil gases. Prior to obtaining samples, blank samples were collected through the copper tubes and analyzed to insure that the tubes were free of volatile organic compounds. By use of the drill to bore a pilot hole, the tubes were inserted into the soil for gas sample collection. Detection and analyses for volatile organic compounds were performed by using a portable field gas chromatographic system, with photoionization detection.

Results of the sampling indicated that as many as 20 different volatile organic compounds could be detected in soil gases above disposal pits on the site. Plots of locations of volatile organic compounds in soil gas indicated two small plumes that extend up to about 50 feet beyond the site to the west and southwest, respectively. No detectable levels of the compounds were found in water or soil gas toward the south, in the direction of ground-water flow in the shallow water-table aquifer.

Key words: soil gas methods, volatile organic compounds, hazardous wastes

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INTRODUCTION

Analyses for volatile organic compounds (VOC) in soil gases have been described by several researchers (1; 2; 3; 4; 5), and methods developed have been applied successfully to many case studies designed to delineate the extent of ground-water contaminations (3; 4; 6). Thompson and Marrin (6) have described in detail the field methods and sampling protocols to properly delineate contaminant plumes. The purpose of this paper is to describe the application of some of these field methods and results of soil gas sampling at a U.S. Environmental Protection Agency Superfund site in carbonate terrain in Middle Tennessee (Figure 1).

In 1978, approximately 44,000 gallons of industrial wastes were disposed in pits on a farm in Williamson County, Tennessee. The waste products, consisted primarily of semi-solid adhesive process waste with some containing solvents, hexane, toluene, chloroethylenes, organic fillers, and water soluble adhesives (7). These were poured into an open pit from a former phosphate strip mine, and four excavated trenches.

Preliminary investigations in 1985 by the State of Tennessee determined the presence of many of these organic compounds in soil and shallow ground water below the site (7). Investigations of the geology in the area (D.B. Withington, U.S. Geological Survey, 1988, written commun.) and hydrogeology (P. Tucci and others, U.S. Geological Survey, 1988, written commun.), and a remedial action investigation (7) have been completed. These investigations have indicated hydrocarbon movement of less than 100 feet in soil and water on the site and in the immediate area surrounding it.

The purpose for studying VOC in soil gas was to locate contaminants and delineate plumes emanating from the disposal site.

HYDROGEOLOGIC SETTING

The surficial geology of the area is composed of 3 to 15 feet of clay-rich regolith, consisting of soil and weathered rock. The underlying correlative Bigby and Cannon Limestones, locally referred to as the Bigby-Cannon Limestone, are underlain by the Hermitage Formation, all of Ordovician age (Figure 2). Below the Hermitage Formation is the Ordovician Carters Limestone, which is underlain by the Lebanon Limestone, also of Ordovician age. The Bigby-Cannon Limestone is exposed on the upper hillslopes, but is not present nor considered a significant aquifer near the disposal site. The principal water-bearing zone affected by the contaminants is the Hermitage aquifer. The lower part of the Hermitage Formation functions as a confining unit to ground-water flow to deeper rocks; thus, the contaminants are confined to the saturated and unsaturated zones of the regolith Hermitage aquifers (P. Tucci and others, U.S. Geological Survey, 1988, written commun.). Hydrologic and chemical data from observation wells indicate that contaminants have not moved appreciably in the regolith Hermitage aquifer neither laterally nor vertically downward to underlying aquifers.

METHODS

Qualitative analyses of VOC from soil gases were performed using a portable gas chromatograph equipped with a photoionization detection system. Separation of the organic compounds was achieved in 1/16-inch columns packed with SE-30 substrate. Organic compounds in ground water from the site were previously identified by laboratory analyses using gas chromatography coupled with mass spectrometry (7). Peaks from the field system were tentatively identified using pure standard samples and comparing retention times of pure compounds with soil gas samples. Individual analyses were conducted at ambient air temperatures (columns were not heated), which varied from 20 °C to 35 °C. Because retention times decrease with increasing ambient temperatures, a benzene standard was periodically injected. The retention time of benzene was used to calculate relative retention times of other standard compounds. Relative retention times were reproducible to within ±5 percent error. Most commonly identified compounds were hexane, trichloroethylene, trichloroethane, toluene, perchloroethylene, and cis and trans dichloroethylene. An example chromatogram is shown in Figure 3.

Sampling of gases from the unsaturated zone was accomplished using two field procedures. The first method employed a 6-foot long hollow steel shaft 3/4 inch in diameter fitted with a carbide twist drill bit. The probe was driven to sampling depth using an electric drill. After flushing the system with at least 10 times its volume of soil gas, the gas was withdrawn through ports located behind the drill head, into stainless steel tubing 1/32-inch diameter inside the shaft and into a gas syringe. Samples were injected into the chromatograph within a few minutes of collection.

This tool was effective during exploration for VOC in soil gas, but proved difficult and time-consuming to decontaminate where large concentrations of VOC were present in the unsaturated zone. In areas where VOC concentrations were greatest, hollow soil probes made of copper tubing were used. The 5/16-inch diameter tubes were 1- to 3-foot long and fashioned with a chisel drive point and four perforations just behind the tip. A pilot hole was bored to within 6 to 12 inches of the sampling depth (usually 3 feet). The copper tube was inserted in the pilot hole and driven into the clay-rich regolith to the proper sampling depth. The flexible tubing from a peristaltic pump was fitted over the top of the copper tube and gas was withdrawn through the length of the copper tube. At least 10 but no more than 100 tubing volumes of soil gas were drawn through this system, and the pump was stopped just prior to insertion of the needle tip of the gas syringe. The needle tip was inserted near the connection of the flexible tubing and the copper tube, and the needle tip pushed past the connection into the top of the copper tubing. The sample was withdrawn and injected into the gas chromatograph within a few minutes of collection.

Because of the persistence of VOC in the soil gas sampling apparatus, it was necessary to decontaminate each part of the sampling system following each positive encounter with VOC in the soil gas. The drill probe and copper tubes were decontaminated with the following procedure--alconox wash, distilled-deionized water rinse, methanol rinse, alconox wash, and distilled-deionized water rinse. The drill probe was further dried by drafting ambient air through the line using a portable peristaltic pump. The tubes were washed in the lab and oven-dried overnight at 150 °C. In the field, both the drill probe and copper tubes were certified free of VOC by drafting ambient air through each and testing each one for VOC contamination, using the gas chromatograph. Gas syringes were similarly washed, rinsed, dried, and certified clean prior to filling with actual soil gas sample. These precautions were essential to the substantiation of the presence or absence of VOC at any sampling location, although some additional field time (about 15 percent) was required by this part of the operation. This procedure was very successful in decontaminating equipment.

RESULTS AND DISCUSSION

Compounds detected in and around the disposal pits are shown on the chromatogram in Figure 3. The most commonly identified compounds showed some variability in relative concentrations, based on measured peak areas, however the overall pattern of compounds or "fingerprint" of the contaminants was consistent in the contaminated areas. On the basis of data collected at about 60 locations, sampled in June and August 1987, and data collected from other site activities (7), the contaminants were found in the area shown in Figure 4. In general, the highest levels of contaminants, as determined from relative responses of soil gas samples in the gas chromatograph-photoionization system, were above the disposal pits, and have been reported to exceed 1,000 parts per million as total volatile organic compounds (7), near the central part of the plume. Ground water has been shown to be contaminated at the site in excess of 100 parts per million total volatile organics, also near the center of the plume (7) (Figure 5).

The shape of a VOC plume in soil gas is determined by many factors including geology, hydrology, topography, chemical nature of the VOC, quantity of VOC present, time since disposal, disposal practices, and the location, size, and shape of the disposal pits. Two lobes of the contaminant plume from the disposal pits extend beyond the fence line to the west. The smaller lobe is in a shallow depression a few inches deep, which extends due west from the disposal pits. The larger lobe extends to the southwest, following the surface drainage pattern. At the lower end of the plume, a drainage channel up to 4 feet deep drains into the south field. At the fence crossing, the south field is about 5 feet lower in altitude than the site itself, and the surface drainage is southwesterly. About 20 soil gas samples from the south field (Figure 5) indicated no VOC present in the unsaturated zone. Samples from ground-water monitor wells in this area showed no detectable concentrations of VOC (7). Movement of the contaminants has been limited to date, but some movement has occurred, principally along surface features of the site. These features may replicate subsurface conditions of fractures or solution channels in the carbonate terrain, which may control ground-water flow and transport of the VOC. In addition to volatilization of VOC into soil gas from contaminated ground water, an alternate contaminant pathway is possible. The presence of the contaminants along the surface drainage channel may be due to runoff washing contaminants from the pit areas into the drainage channel, concentrating them in the soil and soil gas. Furthermore, this indicates the possibility of transport of the contaminants from the site by rainfall saturation of the contaminated soil in the pit areas and overland transport of VOC through the south field and into the Little Harpeth River or possibly into other parts of the shallow ground-water system in the area. Further work is needed to determine the relative importance of these two transport mechanisms. Future investigation of the environmental effects of this site will incorporate these aspects of contamination.

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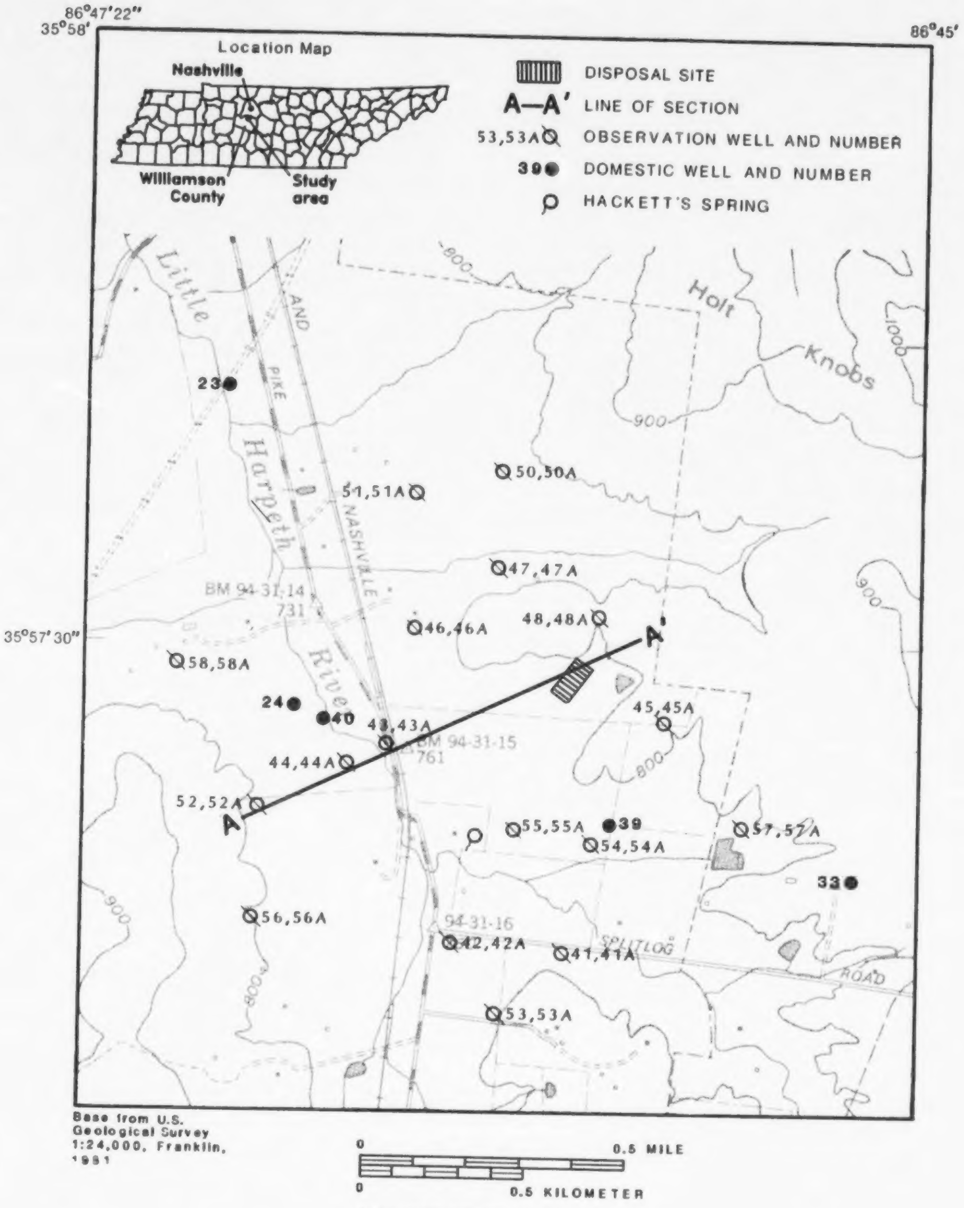

86°47'22"
35°58'
86°45'
35°57'30"
Location Map
Nashville
Williamson County
Study area
DISPOSAL SITE
A—A' LINE OF SECTION
53,53A OBSERVATION WELL AND NUMBER
39 DOMESTIC WELL AND NUMBER
HACKETT'S SPRING
Little Harpeth River
NASHVILLE AND PIKE
Holt Knobs
SPLITLOG ROAD
800
900
1000
BM 94-31-14
731
BM 94-31-15
761
94-31-16
A
A'
23
24
40
39
33
50,50A
51,51A
47,47A
48,48A
46,46A
58,58A
45,45A
43,43A
44,44A
52,52A
55,55A
54,54A
57,57A
56,56A
42,42A
41,41A
53,53A
0
0.5 MILE
0
0.5 KILOMETER

Base from U.S. Geological Survey 1:24,000, Franklin, 1981

CONTOUR INTERVAL 100 FEET
DATUM IS SEA LEVEL

Figure 1.--Location of study area, disposal site, and observation and domestic wells.

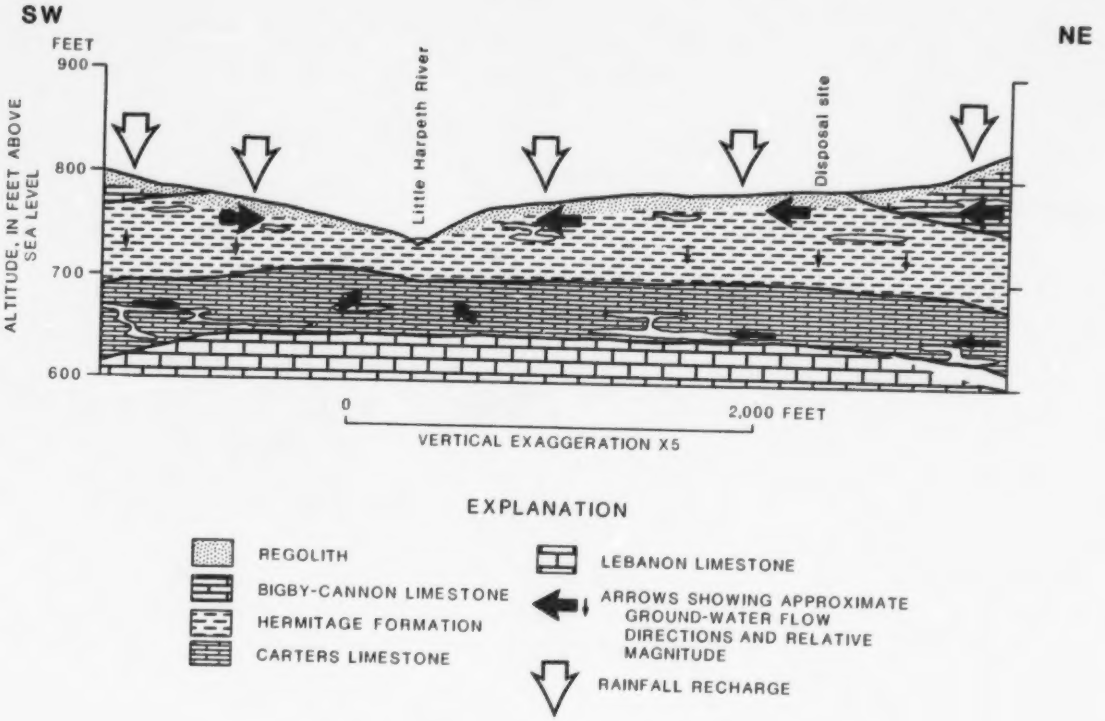

SW
NE
FEET
900
800
700
600
ALTITUDE, IN FEET ABOVE SEA LEVEL
Little Harpeth River
Disposal site
0
2,000 FEET
VERTICAL EXAGGERATION X5
EXPLANATION
REGOLITH
BIGBY-CANNON LIMESTONE
HERMITAGE FORMATION
CARTERS LIMESTONE
LEBANON LIMESTONE
ARROWS SHOWING APPROXIMATE GROUND-WATER FLOW DIRECTIONS AND RELATIVE MAGNITUDE
RAINFALL RECHARGE

Figure 2.--Generalized geohydrologic section of study area.

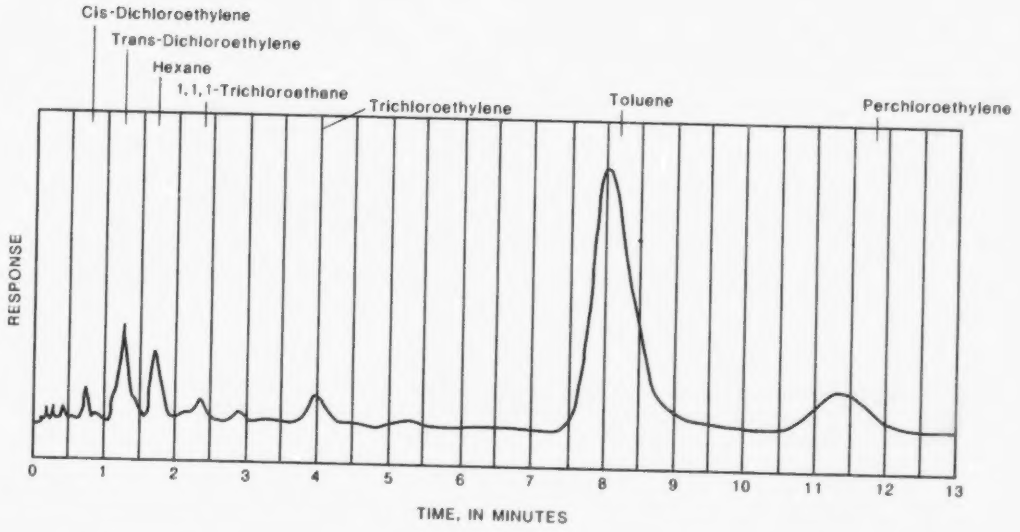


Figure 3.--Chromatogram of volatile organic compounds from soil gas at the hazardous-waste site near Williamson County, Tennessee.

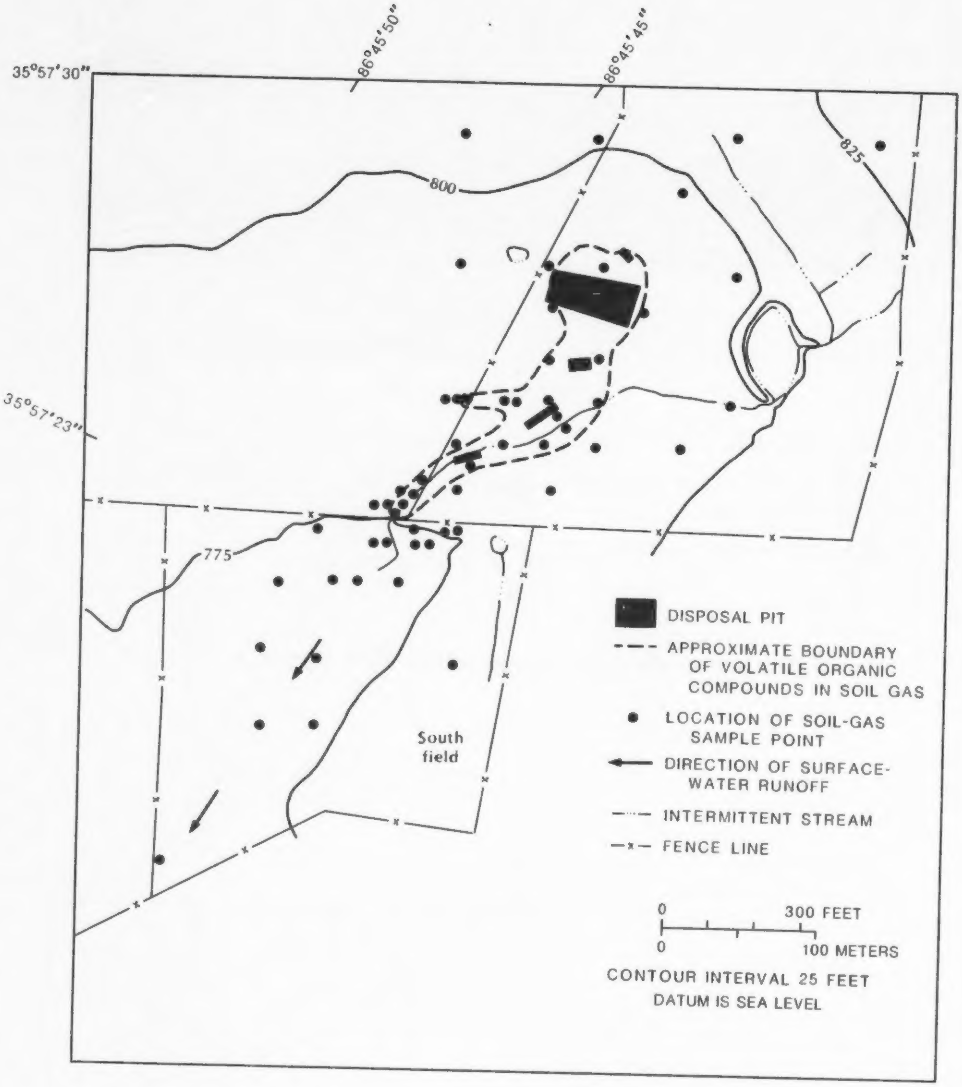
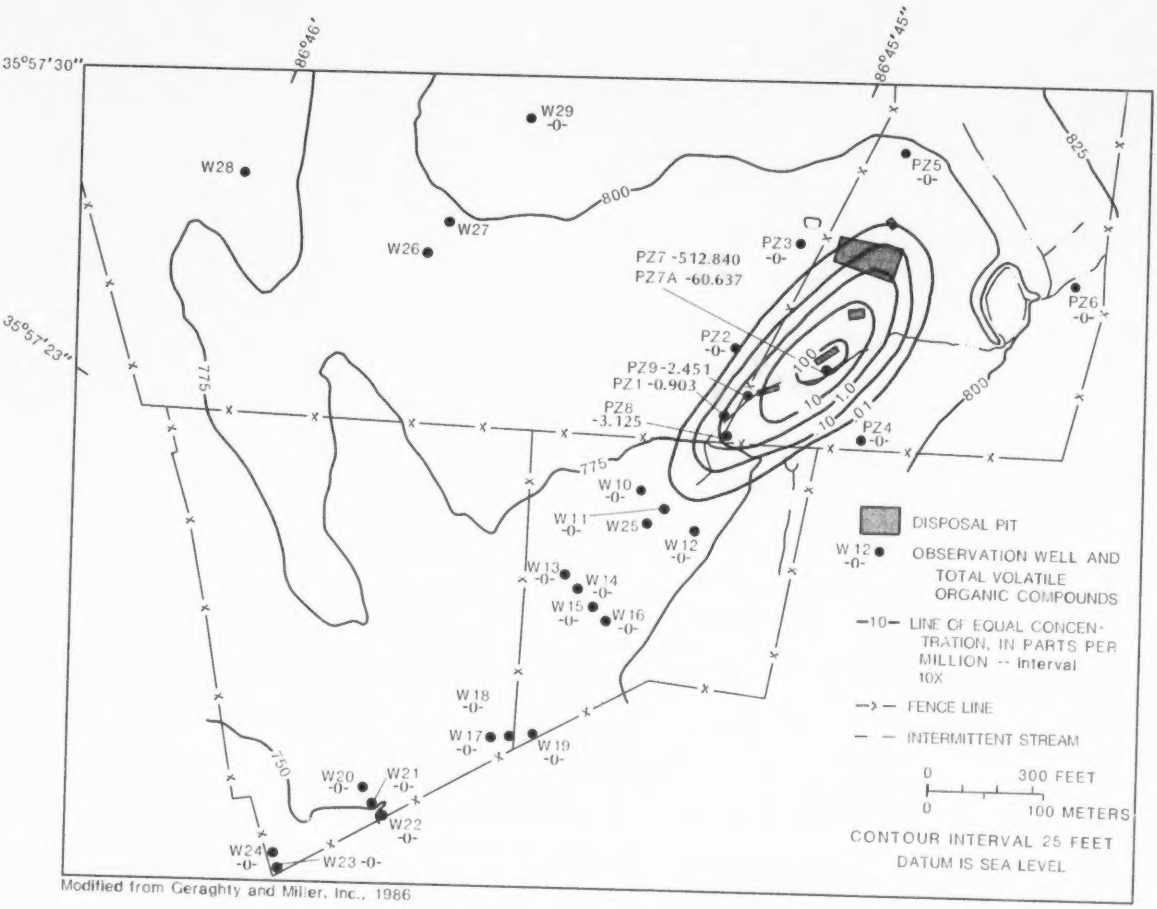

35°57'30"
86°45'50"
86°45'45"
825
800
35°57'23"
775
South field
DISPOSAL PIT
APPROXIMATE BOUNDARY OF VOLATILE ORGANIC COMPOUNDS IN SOIL GAS
LOCATION OF SOIL-GAS SAMPLE POINT
DIRECTION OF SURFACE-WATER RUNOFF
INTERMITTENT STREAM
FENCE LINE
0
300 FEET
0
100 METERS
CONTOUR INTERVAL 25 FEET
DATUM IS SEA LEVEL

Figure 4.--Location of soil-gas sampling points and approximate location of volatile organic compounds in soil gas at the disposal site.


35°57'30"
86°46'
86°45'45"
35°57'23"
W29 -0-
W28
PZ5 -0-
825
800
W27
W26
PZ3 -0-
PZ7 -512.840
PZ7A -60.637
PZ6 -0-
PZ2 -0-
PZ9-2.451
PZ1-0.903
PZ8 -3.125
100
10
1.0
0.1
PZ4 -0-
775
W10 -0-
W11 -0-
W25
W12 -0-
W13 -0-
W14 -0-
W15 -0-
W16 -0-
W18 -0-
W17 -0-
W19 -0-
750
W20 -0-
W21 -0-
W22 -0-
W24 -0-
W23 -0-
DISPOSAL PIT
W 12 -0- OBSERVATION WELL AND TOTAL VOLATILE ORGANIC COMPOUNDS
—10— LINE OF EQUAL CONCENTRATION, IN PARTS PER MILLION -- interval 10X
FENCE LINE
INTERMITTENT STREAM
0 300 FEET
0 100 METERS
CONTOUR INTERVAL 25 FEET
DATUM IS SEA LEVEL

Modified from Geraghty and Miller, Inc., 1986

Figure 5.--Total volatile organics in ground water at the disposal site, April, 1986.

SOIL-GAS SCREENING: ITS THEORY AND APPLICATIONS TO HAZARDOUS WASTE SITE INVESTIGATIONS

Lynne M. Preslo, R. Pavlick and Walter M. Leis
Roy F. Weston, Inc., 1001 Galaxy Way, Suite 107
Concord, California 94520

During the last three to four years, soil-gas sampling has grown from a virtually unknown, seldomly used, technique, to become one of the mainstays and an essential tool in the geosciences field for site investigations. Soil-gas screening, if conducted properly, is a very effective and comparatively inexpensive technique for the following applications:

- *Source-area identification:* Source areas of volatile chemicals within the vadose, or unsaturated, zone can be identified using soil-gas techniques.
- *On-site vs. off-site sources:* Soil-gas can assist in the delineation between on- and off-site sources.
- *Plume-tracking:* Soil-gas screening can be used to track plumes of chemicals within the groundwater, depending upon site conditions.
- *Migration of landfill gases:* Soil-gas screening can also be used to identify the type of chemicals present in and the migration patterns of landfill gases (eg. Calderon Bill Requirements in California).
- *Optimize subsequent monitoring points:* Soil-gas screening is used to optimally locate, and therefore reduce the total number of, the more expensive and more intrusive monitoring points (eg., soil borings and groundwater monitoring wells).

The presentation includes the theory behind soil-gas screening, its applications at various sites and its limitations depending on site conditions.

DISCUSSION

The Preslo et al. paper was not presented at the symposium. The work was summarized by Thomas Spittler, USEPA Region I. The following discussion was then held regarding on-going and future efforts in the soil gas area.

HAL STUBER: A point that ought to be emphasized is that we use a Henry's law constant for the distribution of an organic compound over aqueous solution, whereas there is no such constant over a soil. You can actually have orders of magnitude differences between what you would expect, and what you would get if you spiked a soil today, say with ethylene dibromide, compared to a soil that has been around for 20 years, where the volatilization of the ethylene dibromide is extremely low. You can be misled in that area.

I agree with the value of GC for any kind of specific information. About ten years ago, I worked for the Geological Survey and dealt with a lot of synthetic fuel wastewaters. In particular, the natural groundwaters that I dealt with were about 50 parts per million of organic carbon, with 5% by weight organic material. They are black in color, yet they have virtually no volatiles whatsoever. The GC is blank, almost. GC is incredibly valuable. Anybody doing specific compound plume following should use it, but I would like to see more back-up of that kind of work – the total organic carbon – because there are a lot of nonvolatile things that we might be missing.

THOMAS SPITTLER: Yes, there are a lot of sites where the nonvolatiles far outweigh the volatile constituents. It's also true that at many of these sites, the nonvolatiles have very little inclination or capacity to migrate, and the real problem is the material that has the capacity to migrate that causes problems. For example, you can dump your oil from your car in your backyard from now until doomsday, and if your well is 50 feet away, it probably will never get there. But you put two or three ounces of gasoline into the soil, it will be there in the length of time it takes for rainwater and groundwater to bring it there, and it will be there for a long time to come.

So it is a question of the relative impact. We can have sites contaminated with heavy oil. We can have sites contaminated with PCB's. If it isn't going anyplace, and if a kid isn't sitting there eating it, it has very little health impact.

But a half a gallon of gasoline in that same site could wipe out all of your neighbors' drinking water wells in a matter of a year, or two, or three, depending on the rate of flow.

So the emphasis on the volatiles is fairly well placed. It doesn't mean we are ignoring the others, but in terms of prioritizing and putting our effort where the biggest payoff is, we've got to get a handle on controlling the volatile contamination situations, or we're not going to have enough drinking water around to talk about it.

HAL STUBER: I agree that most of the concern is with the volatiles, the chemicals that we have been emphasizing the most. They are the most toxic and have the greatest mobility.

Just a caution – there definitely are types of compounds, polar, very water soluble organic compounds, that can move in groundwater.

THOMAS SPITTLER: Yes, there are lots of other problems out there. The problem we face, I guess, is a classical problem of limited resources and enormous problems. There is a tendency to throw a lot of money at the problem that's the closest at hand.

HARRY McCARTY: While the oil industry is responsible, in part, for a lot of the problems, particularly with underground storage tanks, a lot of work has been done on soil gas on sniffers, and other techniques for petroleum exploration, even related to oceanographic fields, in terms of off-shore exploration that could benefit to this program. Go beyond some of the classical environmental literature and look at some of the petroleum literature.

Although there is a lot more modern technology, you could apply the same sorts of techniques using more modern instrumentation. You get a lot more information out of it.

The only *caveat* is that the petroleum literature is notoriously slow in coming out, so the techniques you read about this month in the AAPG bulletin were submitted two years ago, and the work was done five years ago. But there is much that could be picked up, and obviously your people have looked at a lot of the problems. Some of the solutions may be found in some of the existing literature as well.

THOMAS SPITTLER: I second that. In fact, I've got a package of articles stacked up on one of my file cabinets that I've sent out to people all over the country. The third article in the package is a historical article that appeared in *Science* about four or five years ago. It's basically a review of the whole halo approach that oil companies used for decades to locate pockets of oil and natural gas great depths in the ground, by simply profiling on the surface, doing vapor monitoring, and finding that there were patterns that were quasi-circular patterns (halo effects) with increasing concentration as you moved into the center. When they got to the center, they drilled right into pockets of oil.

That technology we owe to the oil company, and that's basically where soil gas got its start.

Indeed, we should have a better exchange of newer and more sophisticated technologies when they come up, but the same problem exists with all scientific literature. What's done today will show up three years from now, and what we need is to know what people are doing today, by more verbal exchange, instead of waiting around to read about it as if it were medieval history.

JIM BERYA: In some of our soil gas study areas vapors seem to move laterally above the contamination plume and then collect in pockets. We are driving the probe further down into the ground, plugging the end up with about four, five inches of soil, pulling it out, and analyzing that soil by thin-layer chromatography to look for semi-volatiles and nonvolatile compounds. That confirms the soil gas approach, especially when we are working with JP5 and Jet A samples.

THOMAS SPITTLER: Good observation. There are many geological formations – clay lenses, sand lenses over caliche formations – that are very hard and almost impermeable, so that the vapor, when it migrates, sometimes takes unusual paths.

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You'll find all of these phenomena observed one way or another, directly or indirectly, and people noting that it isn't at all like working out in the middle of a desert, with a totally homogeneous zone. We're dealing with very nonhomogeneous media and problems, and we encounter it at every site. Every site is unique.

TRACIE BILLINGTON: I have been working on an underground tank from a gas station, which happens to be 250 feet away from a drinking water supply well, in an area where the only source of drinking water is groundwater. It's a lot bigger problem than many people perceive. The State of California does have an underground tank program, but site investigations are probably bigger than we can handle.

THOMAS SPITTLER: I spent two hours with a planning commission in southern Rhode Island, which includes six or eight major towns. The whole meeting was centered around what these towns can do to protect their own water supplies.

I started out the session by saying, don't wait for us (EPA). The federal government will not protect your water supplies. The state government will not protect your water supplies. We have, in every state in New England, thousands of towns, each with their own private water supply and millions of private home owners with their own water supply. There is no way we can provide groundwater protection.

We can, however, encourage a strategy that a couple of towns have implemented. Ashton, Massachusetts six or seven years ago bought their own portable gas chromatograph. They hired a Ph.D. chemist (who was one of the early proponents of soil gas monitoring,) on a part-time basis to use that gas chromatograph to do soil gas studies, to study the contamination sources in the town, to monitor around all the gas stations, underground tanks and the principal problem in the town, a big chemical company that had contaminated 40% of their town water supplies. This town has been doing that work for six years. This town knows more about their water supplies, more about where their future problems are going to come from, and more about what they have to do to head off those problems than any place else in the country, and they have done it all on their own. They are the ones who had the water supply problem. And who is a more logical group to do something about it?

These people can't afford a $100,000 van and a GC/MS, but they could afford a $10,000 GC and a part-time chemist, and a space for him to work, the water district headquarters.

It's a perfect example of what can be done. If you want to protect your water supplies, you'd better get together and start doing something about it yourself.

We can give you the help, we can give you the advice, we can give you the technology that's available, we can tell you how to do it, and how not to do it, but we cannot come out and do it for you.

And on the other hand, why should we, if the tools are there, and the willingness is there, and the capability? Take simple gas chromatography. The simpler the tool, the more certain it is you're going to come back with an answer. As soon as the tools get unnecessarily complex (with digitizing, and temperature programming, and computer interfaces, and a telephone link to send the data back) it becomes more difficult to get the sample into the instrument and the chromatogram and standards out.

That's a plea for simplicity, not cheapness. We're talking about good instrumentation with a good track record in the field, but we're not talking about something you can't afford.

In fact, I don't think there is a town in the country that can afford not to do something about the potential contamination of their own water supplies. This is not EPA policy, this is what I think we should be doing and encouraging.

JAMES DELAVIN: How do you educate people to do that? How do you get that kind of information out to people? Can you even consider attending all the town meetings?

THOMAS SPITTLER: I don't know what it takes, really. But I can tell you what I do. I talk about water supply problems to dozens of towns in New England. I have done it in my own town, that has five gas stations sitting only 1,000 yards down gradient. If EPA statistics are correct, that means five leaking underground tanks.

They have been thinking about doing for a year. I think they are ready to act.

PHILIP DURGIN: The people in EPA regions say they need quality assurance guidelines, and our response has been to try and set up a guidance document that deals with quality assurance and quality control. We're going to try to keep it simple, but it will provide some guidance for people who want to have some quality assurance and want to use it in court cases.

THOMAS SPITTLER: Chemists have been doing quality assurance ever since they have been analyzing samples. If you have a good chemist, and he knows what he's doing with the gas chromatograph, he will prepare required standards, and practice quality assurance.

This is not difficult technology. This is relatively simple gas chromatography that requires careful work, good quality control, and proper standardization. Those are not difficult things to achieve. A good guidance document would be most welcome.

ATMOSPHERIC ANALYSIS BY OPEN PATH INFRARED SPECTROSCOPY

Philip L. Hanst

Infrared Analysis, Inc.,
1424 North Central Park Avenue
Anaheim, CA 92802

ABSTRACT

The infrared absorption spectrum of the atmosphere has been recorded with open air paths of 90 meters and 720 meters. A 23 meter long multiple-pass cell was used with a Digilab FTS-40 spectrometer. An MCT detector was used, and spectral resolution was 0.5 cm^{-1}. It is shown that even in the presence of the strong absorption patterns of water and CO_2, pollutant gases may be measured at mixing ratios as low as 10^{-9} (1 PPB). Pollutant gases distort the absorption spectrum of clean air in small but recognizable ways. These distortions are calibrated for quantitative analysis by means of digitized reference spectra. Examples are given for carbon dioxide, methane, nitrous oxide, carbon monoxide, ammonia, difluorodichloromethane, benzene, butane, ethylene, formic acid, formaldehyde, isoprene, methanol, nitrogen dioxide, nitric oxide, nitric acid, sulfur dioxide, ozone and acetone.

INTRODUCTION

The present work is a continuation of long path infrared studies of the atmosphere that have been carried on intermittently for many years. Previous work using long folded optical paths is described in references 1 and 2. These references contain additional citations of previous work.

In earlier work, an enclosed optical path was nearly always used. An exception was the outdoor long path studies by Herget, who used a single long path between large 30-inch transmitting and receiving telescopes. (Reference 3) We now report on open path studies using a three-mirror multiple-pass optical system (White cell), with total optical paths up to one kilometer. At a chosen pathlength, a multiple-pass cell can transmit and re-focus the same amount of energy as a large pair of telescopes, even though the cell mirrors are much smaller than the telescope mirrors. This is the principal advantage of the three mirror cell, as can be inferred from the title of White's original paper in 1942: Long Optical Paths of Large Aperture. (Reference 4)

MEASUREMENT TECHNIQUE

A Digilab FTS-40 spectrometer was used, working with a resolution of 0.5 cm^{-1}. The radiation from the scanning interferometer was projected out the side port of the spectrometer into a 3-mirror multiple-pass cell with a 22.5 meter base path. The two collecting mirrors were semi-circular in shape (D-mirrors). They were cut from a single round mirror of 10 inch diameter. These mirrors were mounted on a pedestal placed in the open air. A wooden cover over the mirrors shaded them from the sun. The field mirror was of 12 inch width and was situated close up against the spectrometer. The cell mirrors were coated with silver, protected with a ceramic over-coating. This type of coating has reflectivity higher than 99% throughout the infrared region. The coating is resistant to tarnish and other types of corrosion. It is superior to gold both in reflectivity and durability.

The arrangement of optical components is diagrammed in Figure 1. The helium-neon laser radiation that originates in the spectrometer and is centered in the infrared beam was found to be bright enough to be seen on the silver mirrors, even in daylight. This red light was used for alignment and pathlength verification. After the infrared radiation had been passed through the long path cell, it was captured and directed to the detector by a 3-mirror transfer optics system mounted on a base plate in the sample compartment. The spectrometer could be returned to normal use merely by removing the transfer optics plate and moving aside the plane mirror that coupled the infrared beam out the side-port. Following are some of the matters considered in the choice of operating conditions.

a. Open Path. If the path is open, there are no wall effects. Reactive compounds are properly measured. Photochemical equilibria are not disturbed. If the air is moving, the trace gas measurements are averaged over all the air mass that moves through the optical path during the time of scanning. Previously, the present author made an effort to surround his light path with an enclosure--a pipe, or some kind of tunnel. One reason for this was to allow recording of a background spectrum when the light path was evacuated or flushed with nitrogen. Another reason was to stabilize the air sample so that refraction effects due to air turbulence would not cause excessive noise in the spectrum. A third reason for the enclosure was to permit filling the light path with water vapor and pure tank air so that a water reference spectrum could be obtained. It now appears that, if necessary, these reasons for enclosing the light path can be ignored.

b. Lack of Noise from Air Turbulence. When there are many cell traversals in an open path, air turbulence causes the red laser beam to move about randomly. The laser beam image at the cell exit shows jitter and pulsations. Probably the infrared image has similar variations. The spectrum, however, does not seem to show noise from this image movement. Probably, this discrimination against the "seeing noise" is due to the high frequencies at which the scan modulates the infrared signal. These modulation frequencies are in the kilocyle range; while the "seeing noise" frequencies are probably ten to one hundred times lower. Low frequency modulations would appear as noise only if one were working in the far infrared.

c. Water Vapor. The concentration of water vapor in the air will be 10^5 to 10^6 times higher than the concentrations of the trace gases being measured. Absorption by water vapor therefore dominates the infrared spectrum. It is customary for spectroscopists either to remove the water from their optical path or to prepare a background spectrum with the same amount of water absorption as in the sample spectrum. Unfortunately, working at kilometer pathlengths complicates preparation of background spectra of water vapor. With the other infrared-absorbing gases, including CO_2, one can fill a relatively small absorption cell with a high pressure of the compound and match the absorption in the kilometer path of air. This is not possible with water, because of its limited vapor pressure. To make a water reference spectrum for a kilometer path, one needs to fill the whole path with water vapor mixed with pure air or nitrogen. This was attempted in previous studies, but not here.

Subtracting the water lines does not add any information to the spectrum; it just makes it easier to read the information that is there. With the kilometer path subtraction being so cumbersome, we have decided to dispense with it. The main thrust of the present work is to show that one can read the spectrum directly for trace gases, without removing any water lines.

d. Resolution. At atmospheric pressure, the width of spectral lines is about 0.2 cm^{-1}. To see all the detail in the air spectrum therefore requires resolving power on the order of 0.1 cm^{-1}. Since the average laboratory FT-IR system does not do that well, a lower resolution must be accepted. Lower resolution is also advantageous in requiring less computer memory and yielding shorter computation times. In the present work, we have used resolution of 0.5 cm^{-1} We have been able to utilize most of the detail in the gas phase spectra while working with our modest-priced instrumentation.

e. Choice of Pathlength. When working in a spectral region where water and CO_2 do not absorb strongly--like the region 1200 cm^{-1} to 800 cm^{-1}--lengthening the optical path increases the measurement sensitivity. When working in a region of strong water and CO_2 absorption, however, the path may need to be shortened to allow transmission of enough energy for a measurement. For some molecules there is a choice between using a strong absorption band that falls in a region of heavy interference, or a weak band that is in the clear. In the case of SO_2, for example, our choice is to use the weak spectral features at 1130 cm^{-1} with a maximum pathlength. In the case of NO_2, our choice is to use the strong band at 1600 cm^{-1}, but to shorten the path to give about 30% transmittance at the measurement frequency.

f. Throughput Advantage of the Multiple-Pass Optical System. Radiation projected by an optical instrument spreads as it goes out. The intensity incident on a distant receiver decreases with the square of the distance from the source. The three-mirror multiple-pass cell brings the collecting mirror close to the source, even though the path is long. This gives the long path of large aperture, with high energy throughput.

g. Convenience of the Multiple-Pass Optical System. The use of a multiple-pass cell allows the transmitter and receiver to be together, as in the present work, where they were part of a commercial spectrometer. The field mirror is mounted with the spectrometer. The objective mirrors are set up as a separate portable unit. A kilometer path can be set up in a room--or on a roof--or in a parking lot. If the spectrometer unit is in a van and the objective mirrors are on a tripod, the whole system can easily be transported from place to place.

h. Choice of Detectors. Any gain in detector sensitivity is equivalent to an increase in pathlength. In spectral regions of strong interference from water or carbon dioide, a gain in detector sentivity is better than an increase in pathlength. A spectrometer system for trace gas analysis should be equipped with a nitrogen-cooled photo-detector of the highest available sensitivity. In the present work, a "wide-band" mercury-cadmium-telluride detector was used. For compounds whose analytical bands fall in the high frequency region--like HF, HCl, and H_2CO--an indium antimonide photodetector should be used.

i. The Background Spectrum. Computer manipulations of the data require that the spectra be in absorbance form. To make an absorbance plot, one needs a background spectrum. In gas studies, the spectrum of the empty cell usually serves as background. Since the open path cell cannot be emptied, we had to resort to "shorting out" the optical system to provide a background spectrum. A pair of plane mirrors did this. One mirror at the entrance to the cell sent the infrared beam across to the other mirror at the cell exit. This second plane mirror sent the infrared beam to the detector. When these background spectra were used with the sample spectra obtained through the multiple-pass cell, the resultant absorbance plots were quite flat across the whole spectrum. This proves that the silver mirrors with their ceramic over-coating do not have any dips in reflectivity in the spectral region used.

j. The Use of Digitized Quantitative Reference Spectra. In recent years the major improvements in infrared technique have come through the computer software. Thirty years ago when the author was engaged in infrared studies of the Los Angeles smog, a transmittance spectrum was obtained from point-to-point hand measurements of the empty cell spectrum and the sample spectrum. The measuring and re-plotting for one transmittance spectrum would take all afternoon. The computer now does this in a second, or less.

The software capabilities now include automated quantitative analysis. For this, one needs digitized quantitative reference spectra, which have not generally been available. Currently available collections of infrared spectra are mainly designed for identification, not quantitation. For quantitative analysis of gases one needs to allow properly for the effects of narrow line widths which lead to deviations from the logarithmic absorption law. In order to avoid those deviations when working at modest resolution, the reference and sample spectra must be used only in the low absorbance region (0.1 or less, for compounds whose spectra have single lines not fully resolved). For the present work a collection of quantitative reference spectra was prepared in digital form using the same instrument that was used for the long path studies. When these spectra are used at low absorbance, the logarithmic absorption law is always obeyed.

THE ATMOSPHERIC TRANSMISSION

Shown in Figures 2 through 5 are the transmittance spectra obtained at a 90 meter path (4 traversals) and a 720 meter path (32 traversals). These spectra were recorded on July 3, 1988, which was a warm but only moderately humid day. These spectra show which spectral regions are available for measurements and which are not.

In Figure 2 we see that even for the shorter path, the region between 3900 cm^{-1} and 3550 cm^{-1} does not transmit enough energy to be of any use. This is the region of the OH bands. Thus alcohols and acids must be detected by bands other than those involving the OH stretch. Likewise, Figure 4 shows that the carbonyl region between 1800 cm^{-1} and 1610 cm^{-1} offers practically no energy, even at the 90 meter path. The detection of carbonyl bands in open air studies is therefore out of the question. This is especially unfortunate, because many strong and characteristic molecular bands fall in the carbonyl region. The region 1580 cm^{-1} to 1400 cm^{-1} is also practically useless, but there are not very many important bands here, so this is not a serious loss.

The plots show that the regions 3200 cm^{-1} to 1800 cm^{-1} and 1400 cm^{-1} to 700 cm^{-1} are the prime spectral regions for open path gas measurements. It will be shown that these open regions of the spectrum reveal bands and lines for almost every polyatomic and hetero-nuclear diatomic molecule in the air. When the revealed band is a strong one, the detection capability extends down to the level of a few parts-per-billion, or lower. When the revealed bands are weaker, the detection limits are correspondingly higher.

EXAMPLES OF TRACE GAS MEASUREMENT

Carbon dioxide is a minor constituent of the atmosphere, but its normal mixing ratio of 340 parts CO_2 per million parts air (PPM) puts its concentration some 200 times higher than the concentration of the next trace gas. Next is methane, at about 1.6 PPM. After methane comes nitrous oxide at 0.3 PPM and carbon monoxide at about 0.16 PPM. Figures 6 and 7 show some of the CO_2, CH_4, N_2O and CO lines that may be used for direct measurements in an open atmospheric path. The lines are of course interspersed with water lines; but some are in the clear and can be used for quantitative measurements. These recommended lines are marked by arrows.

In order to verify our 720 meter pathlength and also to test the validity of our quantitative reference spectra, we have calculated from the spectrum the concentrations of the four naturally occurring molecules mentioned above. To do this we used the Digilab software subtraction routine. To measure a compound, the sample spectrum and the reference spectrum were displayed, and the interactive subtraction was carried out. When the band being displayed was removed from the sample spectrum, the amount was readily calculated from this formula:

$$\frac{\begin{array}{c}\text{conc.-path}\\ \text{product for}\\ \text{reference spec.}\end{array} \times \begin{array}{c}\text{subtraction}\\ \text{factor on}\\ \text{screen}\end{array}}{720\ \text{meters}} = \begin{array}{l}\text{concentration}\\ \text{of compound}\\ \text{in sample}\end{array}$$

The measured values are tabulated below.

Compound	Normal Background (Parts-per-million)	Measured Amount
CO_2	340	350
CH_4	1.6	1.9
N_2O	0.30	0.29
CO	0.16	0.27

The above measured values appear to be an adequate verification of our measurement method. It is especially important to obtain a nearly correct value for N_2O, which is not a pollutant. Previous studies have shown that the N_2O concentration never deviates measurably from its background value.

The low measured value of carbon monoxide indicates that the air mass under study was not polluted by auto exhaust in any significant degree. In an urban area, the CO concentration will usually be about ten times higher than the amount measured here. It appears that on July 3rd, a Sunday, Ossining was not in a plume of pollution moving North from New York City. Instead, it is presumed that the town was immersed in a clean air mass that had moved in from the West with the passage of a weather front during the previous day.

To further illustrate the detection of pollutant gases, we present Figures 8 through 17. In each figure the bottom plot is a portion of the atmospheric spectrum for July 3, 1988. Above is a reference spectrum of the constituent under consideration. The third spectrum presented in each figure is a synthetic spectrum obtained by adding together the atmospheric spectrum and the reference spectrum weighted to correspond to the presence of the indicated number of parts-per-billion (PPB) of the compound. These synthetic spectra therefore show the distortions of the clean air spectrum that are indicative of the presence of pollutants. Particular lines or bands that may be used for quantitative analysis are marked by arrows. These examples cover a number of important molecules, but the set is far from complete. In the future we expect to expand the set of examples to include halogen acids, nitrates, peroxides, nitriles, nitrosamines, alkenes, alkynes, hydrides, organometallics, and other groups of compounds. Discussion of individual cases follows.

Ammonia. Figure 8-left shows that ammonia has several lines and bands favorably located for detection. The two features marked in the figure are probably the best choices for quantitative analysis. Measurement sensitivity is high. The July 3rd spectrum does not show any absorption attributable to ammonia. Comparing the synthetic spectrum with the real spectrum puts the detection limit at 1 or 2 PPB.

Dichlorodifluoromethane. Figure 8-right shows that there is a very strong spectral feature for CF_2Cl_2 at approximately 1161 cm^{-1}. There are some weak N_2O lines in this region, which are barely resolved. We cannot see the CF_2Cl_2 that is present in clean air at about 0.4 PPB. The synthetic spectrum shows that 3 PPA of the compound could easily have been detected. Probably, high spectral resolution would be helpful in detecting the compound at less that 1 PPB.

Benzene. The strongest feature in the benzene spectrum falls at 674 cm^{-1}. This is a region of strong CO_2 absorption and therefore one might consider using a weaker benzene band that falls in a region with less interference. There is such a band centered at 1037 cm^{-1}, but it turns out that this band gives maximum absorbance only 2% as great as the maximum absorbance in the band at 674 cm^{-1}. This is a case where it is best to choose the stronger band and minimize interference by backing off on path length. Figure 9 shows the case for 90 meters of air. There is enough transmission between the CO_2 lines to allow detection of the benzene. The lower spectrum shows that the three absorbance minima centered around 674 cm^{-1} line up nicely in the absence of benzene. In the synthetic spectrum we see that 200 PPB of benzene clearly distorts the pattern in a way that can be used for quantitative measurement.

Butane. Methyl and methylene groups in organic molecules absorb in the region 3000 cm^{-1} to 1850 cm^{-1}--the C-H stretch region. At a 720 meter path the clean air spectrum shows a weak C-H band due to the organic matter. Figure 10 shows how the absorption would be increased if 200 PPB of butane were added to the air. From this synthetic spectrum we determine that the amount of C-H absorption in the July 3rd atmospheric spectrum was equivalent to the absorption by about 50 PPB of butane.

Ethylene. The strongest feature in the ethylene spectrum falls at 950 cm^{-1}, about one cm^{-1} to the side of a water line. At a resolution of 0.5 cm^{-1} a few PPB of ethylene will reveal their presence as a "shoulder" on the water line, as seen in Figure 11-left. In the July 3rd clean air spectrum there is a small shoulder at the bottom of the water line, but this is probably not due entirely to ethylene. There are also weak CO_2 lines in this region, one of which probably contributes to this shoulder. Higher resolution would separate the lines better.

Formic Acid. Formic acid reveals itself in a shoulder on a water line near 1105 cm^{-1} (Figure 11-right). This molecule is a product of the atmospheric photochemistry. The 1105 cm^{-1} band is seen clearly in the spectra of the Los Angeles smog. It has also been observed in spectra recorded through the stratosphere.

Formaldehyde. The C-H stretch band of formaldehyde is rich in lines and falls on the low frequency side of the C-H bands of most other molecules. At a 720 meter path many weak water lines overlap the formaldehyde spectrum, as shown in Figure 12. At least five formaldehyde lines fall between water lines and may be used for measurement. These are marked by arrows. The use of higher resolution and the use of an InSb detector would increase the measurement sensitivity for formaldehyde.

Isoprene. The diolefin isoprene (C_5H_8) shows two strong spectral features near 900 cm^{-1}, one of which is in the clear--Figure 13-left. It is important to be able to measure isoprene in the open air because this compound is released into the atmosphere in large quantities by living and decomposing vegetation.

Methanol. Methanol, Figure 13-right, is measured with good sensitivity by its sharp spectral feature at 932 cm^{-1}. Because of the use of methanol in gasoline, the compound is now regularly detected in the urban air.

Nitrogen Dioxide. NO_2 measurement is a case where it is necessary to back off on pathlength so that its major band may be seen through the water interference. This is shown in Figure 14-left. At 90 meters path there is a small "window" at 1600 cm^{-1} that shows some of the structure due to the NO_2 band. There is structure in the spectrum of the atmosphere on July 3rd that corresponds to perhaps 30 PPB of NO_2. The synthetic spectrum shows the deepening of the structure when 100 PPB of NO_2 are added. The use of higher spectral resolution would probably make the detection of NO_2 easier.

Nitric Oxide. NO, like NO_2, must been seen through water interference. With NO, the interference is less, so the 720 meter path has been used. The absorption coefficient for NO is much smaller than the absorption coefficient for NO_2, so that the detectability levels of the two molecules turn out to be about the same. Figure 14-right shows the appearance of an NO "line" at 1900 cm^{-1}. This line is in fact an unresolved doublet, so here again is a case where higher resolution would benefit the detection.

Nitric Acid. For nitric acid measurement we choose spectral features of moderate strength that fall in the region 900 cm^{-1} to 880 cm^{-1} (Figure 15-left). There are stronger features in the nitric acid spectrum, but they are not in the clear. The arrows indicate two features suitable for quantitative analysis. After seeing the distortion due to 20 PPB of HNO_3, one can look back at the "clean air" spectrum of July 3rd and conclude that it contains absorption due to approximately 5 PPB of HNO_3.

Sulfur Dioxide. Unfortunately, the strongest SO_2 band, centered at 1360 cm^{-1}, is well into the main water band. In measuring SO_2 we must therefore rely on the relatively weak spectral features between 1200 cm^{-1} and 1100 cm^{-1}. Bands useful for quantitative analysis are marked in Figure 15-right. The amount of SO_2 used for the example was relatively high--500 PPB. Increases in sensitivity are available from using a long scanning time, a longer path and a more sensitive "narrow band" MCT detector.

Ozone. Ozone detection is straightforward, as shown in Figure 16. The clean air spectrum of July 3rd showed absorption due to about 30 PPB of ozone.

Acetone. The last example--for acetone--Figure 17, shows that compounds with broad bands are detectable, but generally with less sensitivity than compounds with sharp features. Acetone is a poor case for infrared open path work because its very strong carbonyl band is hidden by water.

ACKNOWEDGEMENT

The assistance of Mr. Jeffrey D. Bernson in the experimental portion of this work is gratefully acknowledged.

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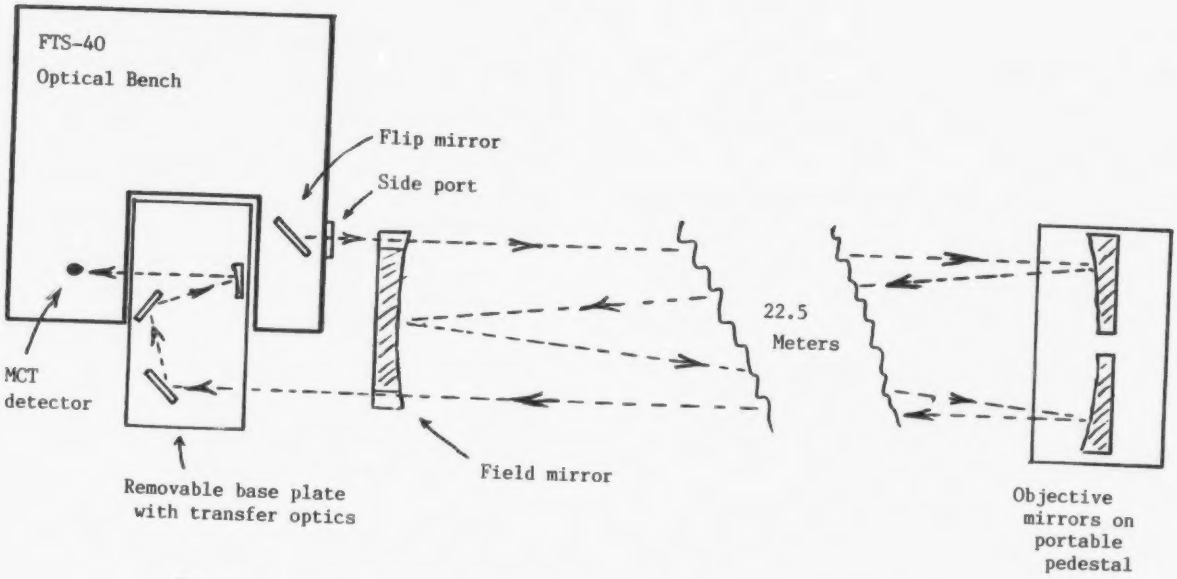

FTS-40
Optical Bench
Flip mirror
Side port
MCT detector
Removable base plate with transfer optics
Field mirror
22.5 Meters
Objective mirrors on portable pedestal

Figure 1. Optical system for open air long path infrared spectroscopy.

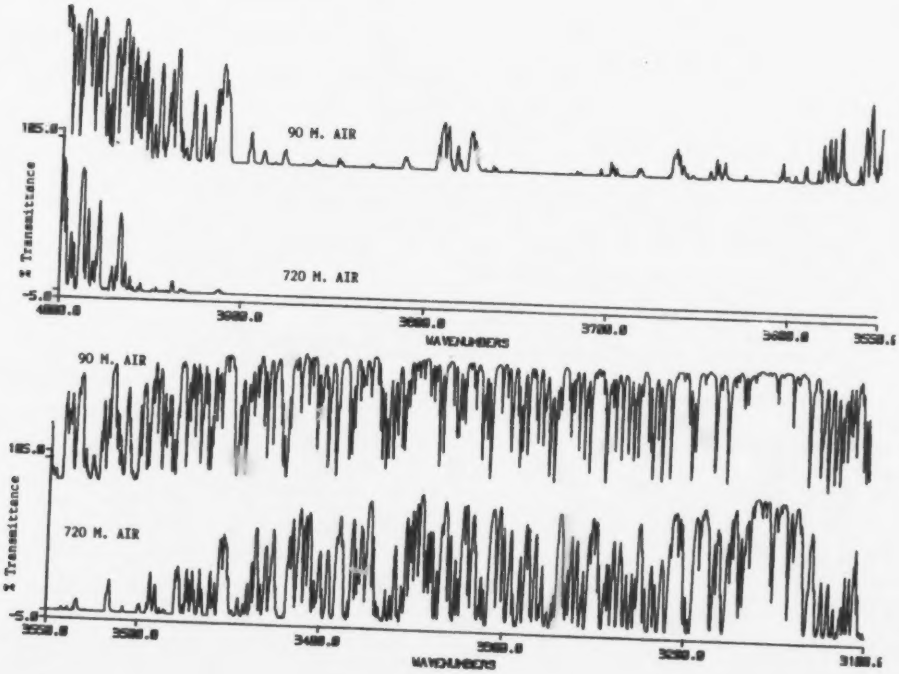


Figure 2. Infrared transmittance of air at Ossining, New York - July 3, 1988.
Digilab FTS-40 spectrometer - MCT detector - 0.5 cm^{-1} resolution - 30 minute scan.

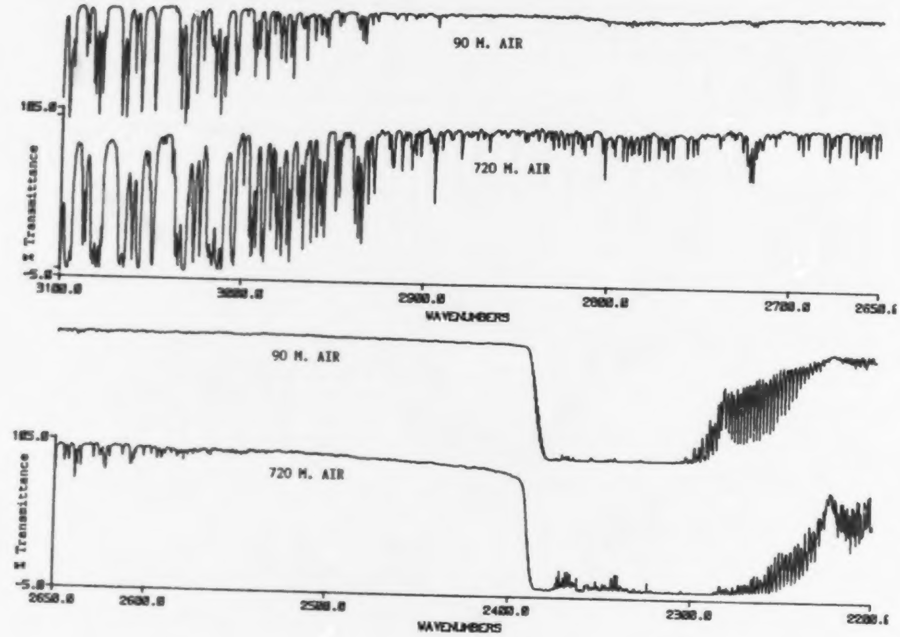


Figure 3. Infrared transmittance of air at Ossining, New York - July 3, 1988.
Digilab FTS-40 spectrometer - MCT detector - 0.5 cm^{-1} resolution - 30 minute scan.

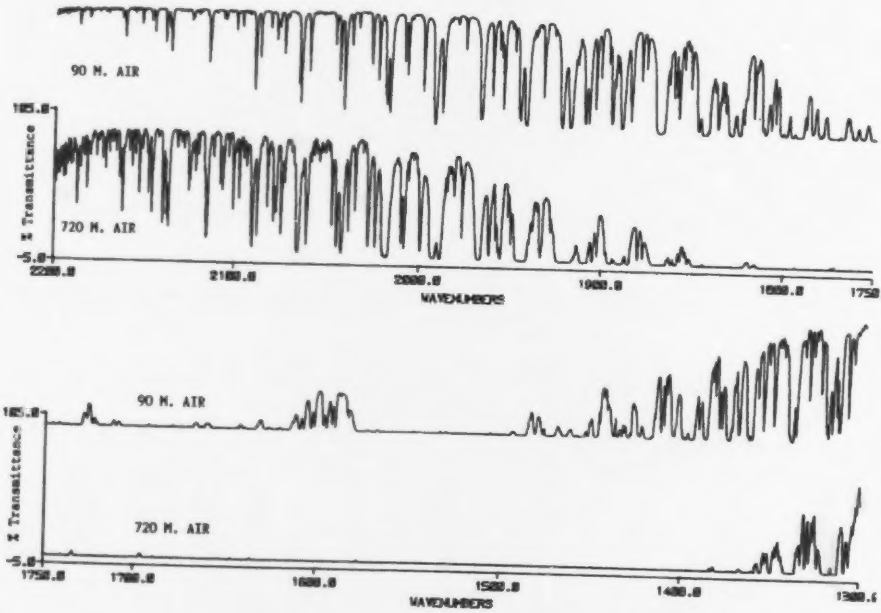


Figure 4. Infrared transmittance of air at Ossining, New York - July 3, 1988.
Digilab FTS-40 spectrometer - MCT detector - 0.5 cm^{-1} resolution - 30 minute scan.

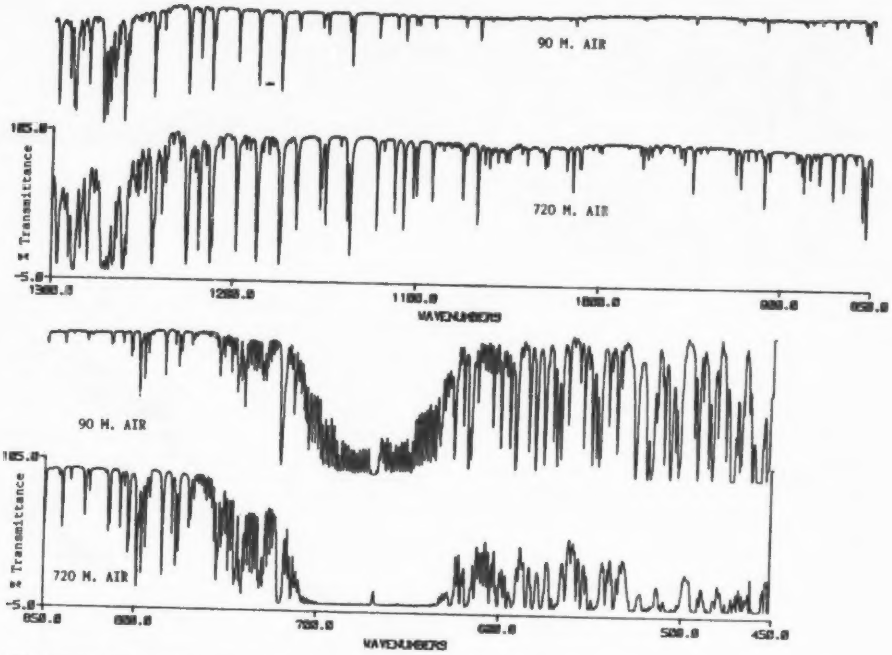


Figure 5. Infrared transmittance of air at Ossining, New York - July 3, 1988.
Digilab FTS-40 spectrometer - MCT detector - 0.5 cm^{-1} resolution - 30 minute scan.

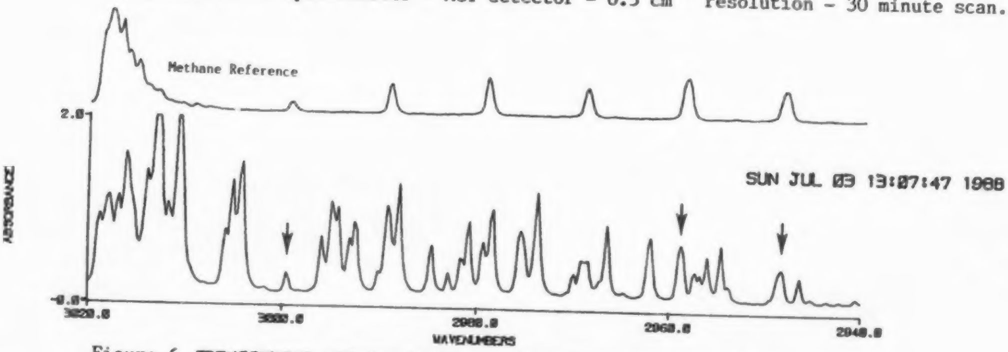


Figure 6. IDENTIFYING METHANE LINES - 720 METERS AIR - METHANE REFERENCE

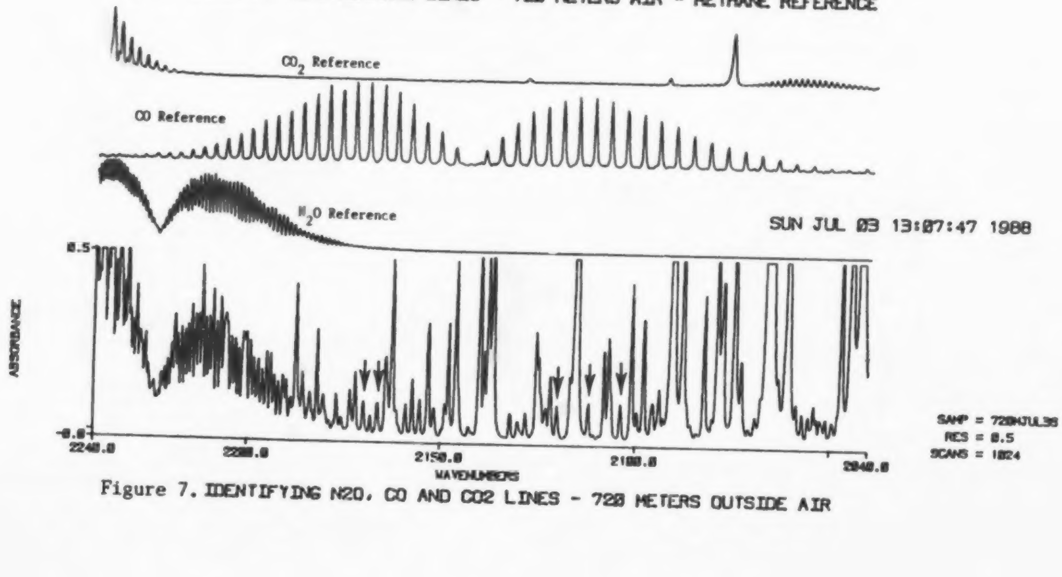
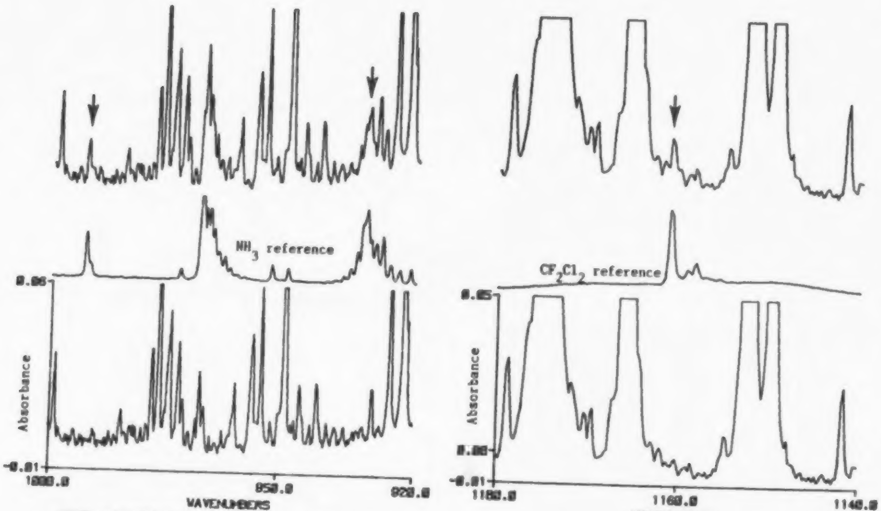


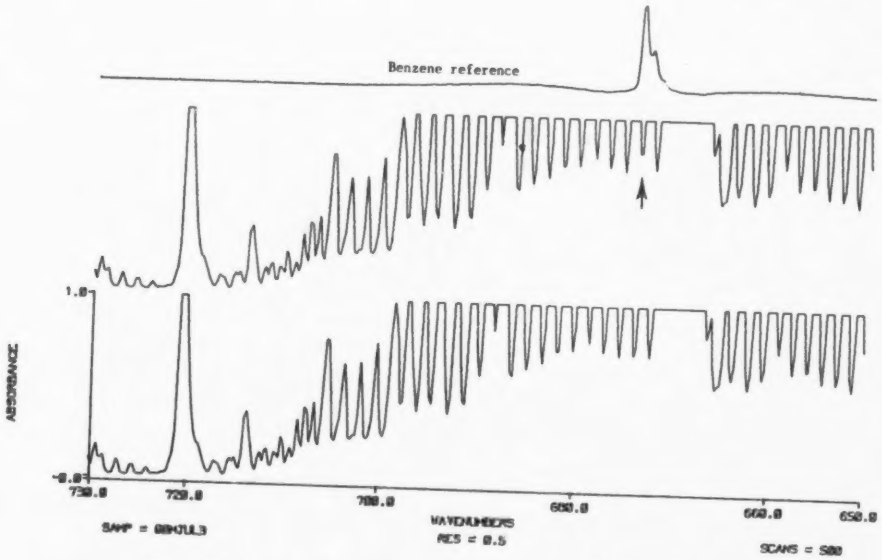
Figure 7. IDENTIFYING N2O, CO AND CO2 LINES - 720 METERS OUTSIDE AIR



SAMP = 720MJUL3 RES = 0.5 SCANS = 1024
ADD 20 PPB AMMONIA TO 720 M AIR
SUN JUL 03 13:07:47 1988

SAMP = 720MJUL3 RES = 0.5 SCANS = 1024
ADD 3 PPB CF2CL2 TO 720 M AIR
SUN JUL 03 13:07:47 1988

Figure 8. Ammonia and Difluorodichloromethane.



SAMP = 80MJUL3
RES = 0.5
SCANS = 500

80 M AIR - 80 M AIR WITH 200 PPB BENZENE - BENZENE REFERENCE
SUN JUL 03 15:00:26 1988

Figure 9. Benzene

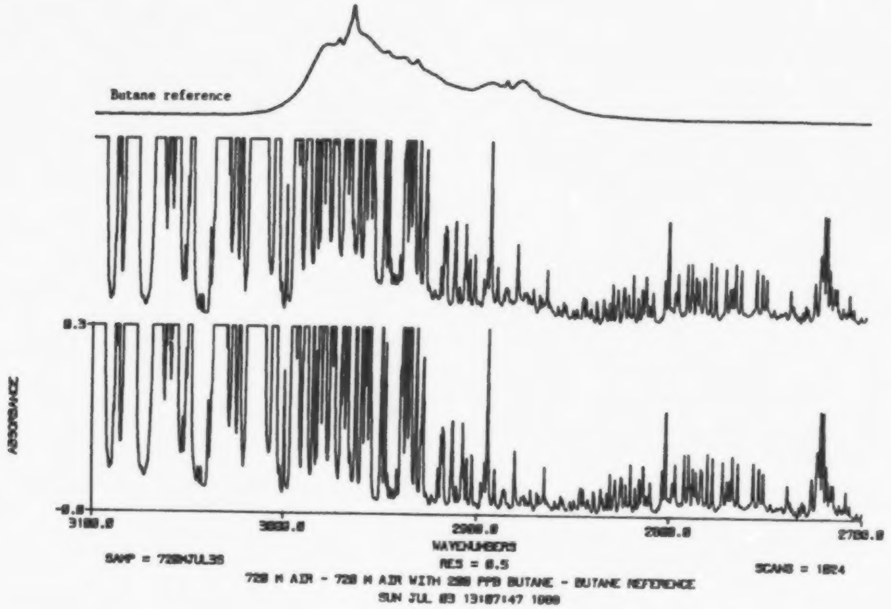


Figure 10. Butane.

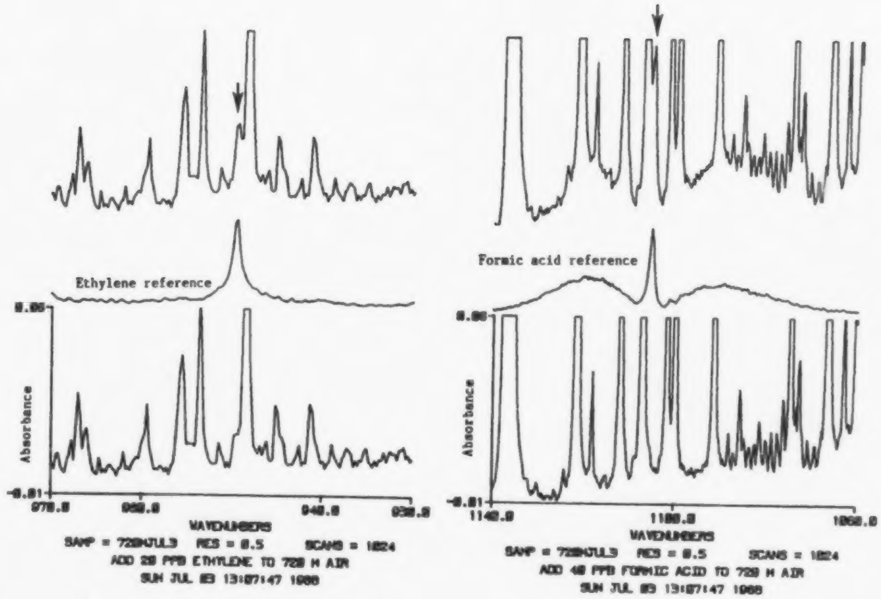


Figure 11. Ethylene and Formic Acid

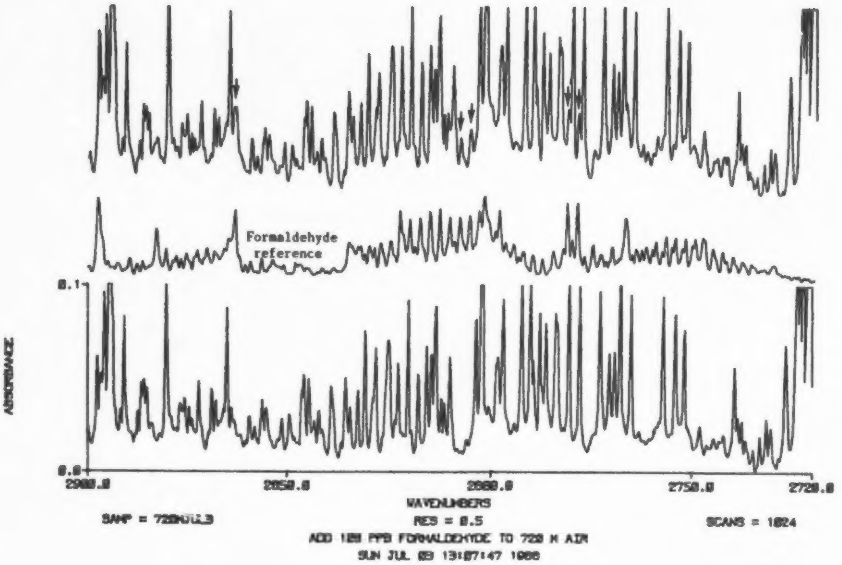


Figure 12. Formaldehyde.

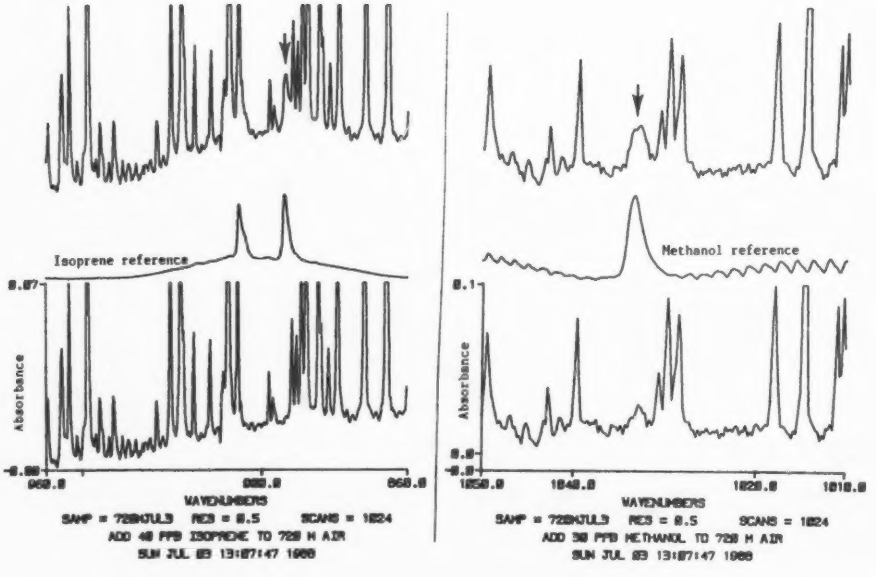


Figure 13. Isoprene and Methanol.

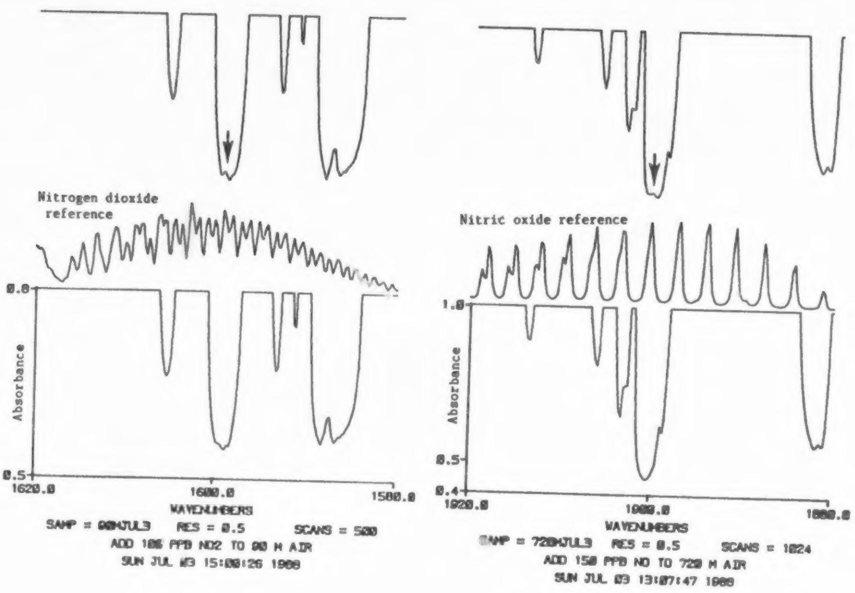


Figure 14. Nitrogen Dioxide and Nitric Oxide.

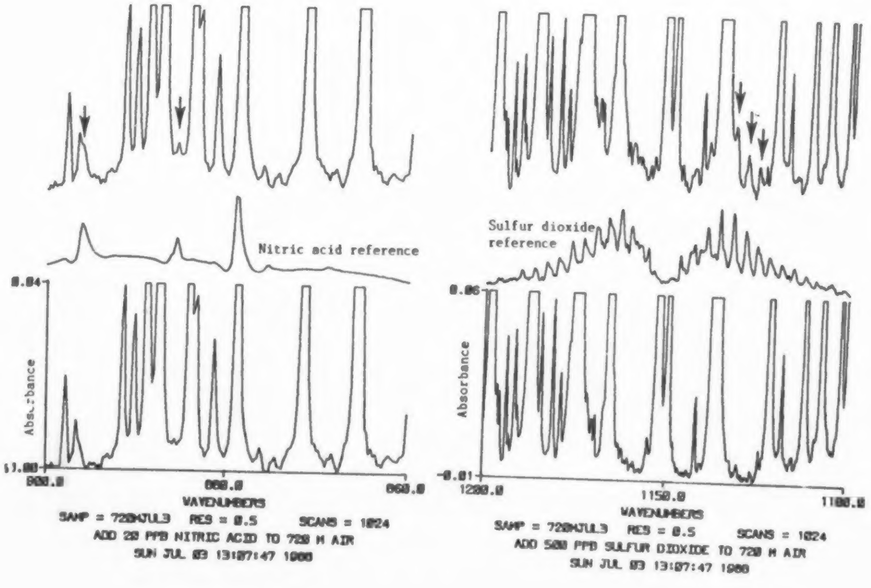


Figure 15. Nitric Acid and Sulfur Dioxide

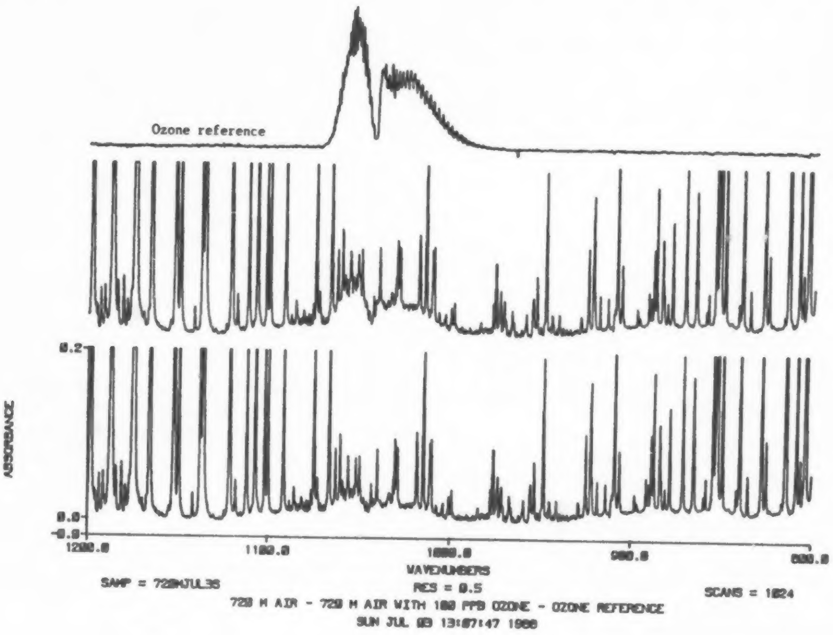


Figure 16. Ozone

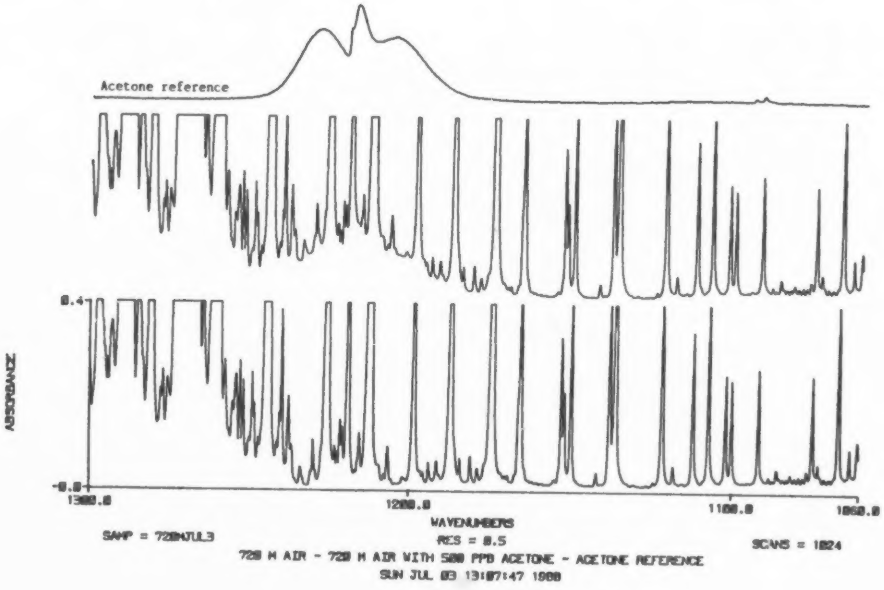


Figure 17. Acetone

DISCUSSION

JOSEPH SOROKA: How careful do you have to be in subtracting your reference or your clean air spectra from your actual spectra. In work that I'm familiar with, subtraction has been a very sticky problem especially determining when you've reached a point where you've subtracted enough and not too much.

PHILIP HANST: With the interactive subtraction, you have computer control. You subtract very slowly, and the subtraction factor appears on the screen continuously, so when you have finished subtraction, you get that number. Divide it by your path length, and there's the answer in parts per million – that is, if you have a reliable reference spectrum proper for quantitative work.

There are collections of thousands of infrared spectra, and they're made only for a qualitative analysis. They're not designed for quantitative work. Always use the strongest band for your measurement, because that's where you get sensitivity. If you look at published spectra, the strong bands usually bottom out. They're too intense, and they deviate from Beer's law for various reasons, which prohibits using those spectra for quantitative analysis. So you have to make your own reference spectra and keep the absorbance very low. You use the MCT detector, so you have a good signal to noise ratio. You don't let the absorbance of any bands go above say, 0.1. Then you have a quantitative reference spectrum that you can believe in, which follows Beer's law. You read the subtraction factor off your screen, and you have your answer.

I have a Digital Lab spectrometer. We're working together, preparing a library of quantitative reference spectra for gas analysis that are digitized, and available on floppy disk. You can get them and do the same thing that I've done.

JOE SOROKA: Would you estimate that a different operator on the same instrument, for example, or on a different instrument, would be able to do the kind of analysis you are doing relatively easily?

PHILIP HANST: Yes. You wouldn't have to know spectroscopy. I think the software has made it so easy that as soon as you learn what to look for, anyone can do it. The quantitative correct answer can be obtained down to a part per billion level.

JOE SOROKA: Do you feel confident that you've hit most of the known possible components in the air, that you're not going to get any interferences?

PHILIP HANST: From experience, there are half a dozen important pollutants. Usually, the strong lines of bands are at different places in the spectrum. Overlap and interference between the trace gases hardly ever comes up. It's the interference between the water and the trace gases that you're always fighting.

DEVELOPMENT OF THE MINITMASS, A MOBILE TANDEM MASS SPECTROMETER FOR MONITORING VAPORS AND PARTICULATE MATTER IN AIR

Henk L.C. Meuzelaar, William H. McClennen, Neil S. Arnold
Tim K. Reynolds, Wallace Maswadeh, Patrick R. Jones and Dale T. Urban

Center for Micro-Analysis and Reaction Chemistry
University of Utah, EMRL, Room 214
Salt Lake City, Utah 84112

ABSTRACT

A fieldable, miniaturized Ion Trap Mass Spectrometer (MINITMASS), based on a Finnigan MAT ITMS system, was developed and tested. In addition to regular electron ionization, the MINITMASS is capable of operating in chemical ionization as well as collision-induced dissociation modes and features selective mass storage and axial modulation options.

A specially designed air sampling inlet allows direct analysis of permanent gases and condensable vapors. A limited amount of chromatographic pre-separation can be obtained by means of "transfer line chromatography". Furthermore, a novel electrostatic aerosol sampling inlet has been developed which deposits air particulate matter on Curie-point pyrolysis filaments thereby enabling subsequent desorption of adsorbed volatiles and/or pyroylsis of nonvolatile organic matter.

The MINITMASS weighs less than 115 kg, uses approx 1000 W and fits into a single electronic rack. A 8x7x7 ft mobile laboratory module, which can be transported with a regular 3/4 ton pick-up truck, provides access to remote test sites and enables operation under demanding environmental conditions. Moreover, the MINITMASS system can be remotely controlled from distances up to several miles, thus facilitating operation under hazardous conditions.

Preliminary test results with three model compounds, namely a permanent gas (sulfur hexafluoride), a condensable vapor (diethyl malonate) and a biological aerosol (bovine serum albumen), illustrate the special capabilities of the MINITMASS system.

KEYWORDS: fieldable mass spectrometer; tandem mass spectrometry; chemical ionization; direct air sampling; transfer line chromatography; aerosol characterization; mobile laboratory module; remote control; Curie-point pyrolysis.

INTRODUCTION

Highly desirable characteristics of fieldable mass spectrometry (MS) systems for hazardous waste site investigations include high sensitivity and specificity, in addition to real-time analysis capability and user-friendliness. Furthermore, the system should be versatile enough to handle a broad range of different sample types, i.e., gases, liquids and solids. Preferably, all this should be embodied in a small, lightweight, ruggedized and affordable instrument package.

No system reported combines all of the above desirable characteristics. Instead, common trade-offs involve: specificity vs. size, weight and cost (viz. in tandem MS systems (1)); specificity vs. real-time analysis (viz. in GC/MS systems (2)); or sensitivity vs. real-time analysis (e.g., in purge-and-trap systems (3)).

Recent advances in Ion Trap MS technology (4) now open up the possibility of designing powerful tandem MS systems with chemical ionization capabilities without compromising size and weight requirements. Moreover, a novel direct air sampling technique developed in our laboratory and based on the so-called "transfer line gas chromatography" (TLGC) approach can provide sub ppm detection levels in combination with enhanced specificity while keeping response times low. Finally, a unique on-line aerosol sampling inlet has been developed which enables characterization of nonvolatile organic components in air particulate matter or of adsorbed volatile constituents.

Preliminary test results obtained with the MINITMASS, a miniaturized Ion Trap mass spectrometer equipped with specially designed inlets for direct air sampling as well as aerosol collection, will be reported here.

INSTRUMENTATION

The MINITMASS is an Ion Trap MS based instrument capable of operating in Chemical Ionization (CI) (5), Collision Induced Dissociation (MS^n) (6) and Selective Mass Storage (SMS) (7) modes. Further, it has the advanced capabilities of

Automatic Gain Control (AGC) (8), Automatic Reaction Control CI (ARC-CI) (9) and Axial Modulation (AM) (7).

In normal scanning electron ionization mode, Finnigan MAT Ion Trap Detectors are specified to measure 1 ng of naphthalene with a 30:1 S/N ratio (10). Use of the above described special operational modes can substantially improve minimum detectable quantity levels (complete mass spectra have been reported from subpicogram sample quantities (11) using CI), as well as dynamic range (AGC and ARC-CI) and specificity (MS^n and CI). The new SMS and AM modes are especially powerful for trace analysis in complex sample matrices while also enhancing overall sensitivity (12).

The complete MS system with vacuum pumps and COMPAQ 386/20 microcomputer workstation weighs less than 115 kg, uses approx. 1000 W of electrical power and can be installed in a single 1.5 m high electronic rack (see Figure 1). This rack also accomodates all gas cylinders (carrier gas + CI reagent gases) as well as the power supplies and control electronics for the vapor and aerosol sampling inlets.

Vapor and Aerosol Sampling

Figure 2 shows the vapor and aerosol sampling inlets, both of which have been specially designed at the University of Utah. Since some technological innovations incorporated in each inlet are currently being patented, only a general description follows here. The vapor sampling inlet (Figure 2a) can be heated to 523 K to eliminate condensation losses of low volatile atmospheric components and connects directly to a standard 1 m capillary transfer line available on all Finnigan MAT ITD systems. During sampling a short 1-4 s "pulse" of ambient air is admitted into the capillary transfer line at 15-30 s intervals. Between sampling the inlet is sealed off dynamically by a curtain of inert gas.

The aerosol sampling inlet shown in Figure 2b consists of a pump drawing 0.1 l/s of air through an electrostatic charging section into an electrostatic precipitation zone where charged aerosol particles are deposited on the tip of an 0.5 mm dia. ferromagnetic filament. After a predetermined collection period, the filament is mechanically drawn into a sealed-off reactor where it is rapidly heated by means of a 500 kHz rf field. This so-called Curie-point pyrolysis technique has been described in detail elsewhere (13). Evaporation and/or pyrolysis products formed are sucked into the heated capillary transfer line and transported into the vacuum chamber of the MS system.

Automation and Data Processing

The basic ion trap MS system is controlled by standard Finnigan MAT software (ITMS, revision B) to which we have added several routines for automation of sampling inlet functions and CI gas control. After initial set-up, the complete system can be remotely operated from a distance of up to several kilometers using twisted pair wire connections, high speed (60 kbaud) line drivers and commercially available Carbon Copy Plus (Meridian Technologies) software, and a second PC-AT compatible computer work station. Figure 3 shows a block diagram of the various control systems. Besides enabling operation of the MINITMASS in hostile environments, one of the main benefits of operation under Carbon Copy Plus is that this allows transfer of data to remote computer stations while new data are still being acquired by the local work station.

Final data processing of complex signals, e.g., obtained in the presence of chemical interferents and/or background signals, can be performed by means of SIGMA-PC, a special software package for multivariate statistical analysis of spectroscopic data developed at the University of Utah. SIGMA-PC is a new PC compatible version of the SIGMA program originally written for IBM 9000 workstations and described elsewhere (14). Major subroutines of SIGMA-PC include: normalization, univariate analysis, factor analysis, discriminant analysis, canonical correlation analysis, variance diagram, K nearest neighbor classification and various graphic routines for visualizing spectroscopic data.

Mobile Laboratory Module

In order to enable field-operation of the MINITMASS while providing the basic amenities of an instrumentation laboratory, we have designed and constructed a 10 m^3 lab module which fits the bed of a regular 3/4 ton pick-up truck (see Figure 4). An aluminum/polystyrene sandwich construction minimizes total weight while providing excellent insulating properties. The mobile lab module has several functions. First of all, it provides physical support for the MINITMASS system and associated sampling inlets. Moreover, it is equipped with a battery (12 V, 500 Amp hrs) powered 110 V ac power supply capable of supporting MINITMASS operation for up to 4 hrs. Further, a 3.5 kW (generator powered) air conditioning system enables operation in hot environments (up to 309 K tested).

Also, dual propane tanks allow up to 1 week of freezer operation (sample and solvent storage), as well as for gas heater and cooking stove use. Finally, the mobile lab module provides adequate working and living space for 2 technicians and, when necessary, rudimentary sleeping quarters.

EXPERIMENTAL CONDITIONS

Vapor sampling data reported here were obtained under the following conditions. SF_6 vapors were diluted into a six gallon bucket inverted over the vapor sampling inlet. The dilution produced a sample concentraton of approx. 40 ppm which was analyzed with an EI scan function utilizing the SMS capability of the system. The m/z 127 ion was isolated and the resulting ions scanned from 60 to 150 u. Ionization time was

2000 msec and the scan rate was 4 s^{-1}. Vapors were sampled repetitively for 2 s each while the volumetric flow into the instrument was 0.025 ml s^{-1}. The vapor inlet and transfer line were operated at ambient temperature (approx. 300 K).

Diethyl malonate (DEM) data were obtained by a H_2O-CI-MS/MS method. The sample was ionized for 3 ms and allowed to react with the H_2O reagent gas for 100 ms before isolating the m/z 161 parent ion. After 5 ms of collision-induced dissociation the daughter fragments were scanned from 60-200 u. Sampling times were approximately 4 s each with the helium flow into the instrument set at 0.02 ml s^{-1}. The transfer line and inlet temperatures were set at 373 K.

Bovine serum albumin (BSA) aerosol sampling data were obtained from aerosols produced in a laboratory nebulizer from a solution of 1 mg/ml BSA in water. The aerosols were collected electrostatically onto a 1040 K Curie-point pyrolysis wire for 11 minutes and then pyrolyzed for 1.5 sec. The inlet was heated to 473 K and the transfer line was operated at 433 K. A 2:1 split of pyrolysis products entered the transfer line. Data were obtained using a standard AGC scan function. The scan rate was 4 s^{-1} from 50-200 u.

PRELIMINARY TEST RESULTS

Sulfur hexafluoride (SF_6) is a frequently used leak detection and environmental tracer gas. Figure 5 shows three repetitive samples of 40 parts per million (ppm) levels of SF_6 in air. For this sequence the samples were taken every 15 s although the very short elution time on the capillary in the TLGC would allow sampling intervals as short as 5 s. The SF_6 is detected easily with electron ionization (EI) due to a very strong SF_5+ ion at m/z 127 which carries over 80% of the ion intensity. However, since this positive ion is very stable, there is little or no specificity gain when operating in the MS^n mode.

Diethyl malonate (DEM) was chosen as a test chemical for field tests simulating compounds with relatively high boiling points and low vapor pressures. This organic compound with a boiling point of 471 K fragmented readily and produced the positive ion spectra shown in Figure 6 using EI, H_2O-CI, SMS and MS/MS, respectively. The EI spectrum in Figure 6a shows characteristic fragments at m/z 133, 115, 105 and 87 with a very small amount of the molecular ion at m/z 160 except when self-CI takes place at high concentrations. The H_2O-CI (Figure 6b) gives an abundant $(M+H)^+$ ion at m/z 161, but still shows some of the characteristic fragments. The SMS function (Figure 6c) enhances sensitivity by allowing all ions outside a predefined narrow mass range of interest to be dumped from an overfilled trap prior to the analytical ion scan. MS/MS on the ion signal of interest (Figure 6d) then regains the selectivity and specificity of the fragment ions.

Transfer line chromatograms from the repetitive analysis of DEM vapors are shown in Figure 7 using H_2O-CI-MS/MS (as in Figure 6d). For these samples, a 1 ml/min stream of saturated DEM vapor in air at ambient temperature was dilated in a larger air stream (72ml/min) to give a final concentration of approximately 6 ppm. The chromatogram traces of m/z 115 and 133 show the strong specific ions from the DEM each with a signal to noise greater than 100.

An example of biological aerosol analysis is demonstrated in Figure 8. In Figure 8 the BSA solution has been aerosolized, collected by electrostatic precipitation on the Curie-point wire, and then analyzed by Py-TLGC. This data represents approximately 150 ng of BSA collected over 8 min and analyzed by a TLGC run of 30-40 s duration. The ion chromatogram profiles in Figure 8 are believed to represent amino acid dimers similar to the structure shown. Further interpretation of these ion signals, currently underway in our laboratory, will be greatly aided by MS/MS daughter ion spectra. Moreover, several critical parameters for aerosol collection require further optimization to improve on what is presently estimated to be only a 2-3 % aerosol collection efficiency. However, these results clearly demonstrate the wealth of sample specific information produced by our TLGC technique on a very short time scale when analyzing complex vapor or aerosol samples.

CONCLUSIONS

The data presented here demonstrate the feasibility of constructing a fieldable MS system, with MS^n, CI and other advanced capabilities while meeting size, weight and power requirements compatible with transportability to remote or otherwise less accessible test sites.

Specially designed vapor and aerosol sampling inlets can be directly connected to the MS system by means of a heated capillary transfer line which provides a definite amount of chromatographic separation, thereby increasing specificity while maintaining short response times. Moreover, our novel direct vapor inlet technique has been shown to produce sharp air "injection" peaks, thereby enabling optimum use of the TLGC approach, whereas the aerosol inlet has been demonstrated to produce characteristic pyrolysis fragments of complex organic aerosol components.

A relatively high degree of automation has been achieved which enables operation of the entire system from remote computer workstations up to several miles away, e.g., when performing vapor and aerosol analyses in hostile environments.

Also, a 10 m^3 mobile lab module was constructed which has proven to be a suitable operating base for the MINITMASS under demanding environmental conditions while providing accessibility to off-road test sites using a regular 3/4 ton pick-up truck vehicle.

Present shortcomings of the MINITMASS include: (a) inability to move the system during operation (due to the presence of a turbomolecular vacuum pump) and (b) low collection efficiency of the aerosol inlet (probably due to incomplete optimization).

ACKNOWLEDGEMENTS

Credit is given to Finnigan MAT Corporation (San Jose, CA), Geocenters, Inc. (contract #GC-1728-88-002) and to the Advanced Combustion Engineering Research Center (funds for this Center are received from the National Science Foundation, the State of Utah, 23 industrial participants, and the U.S. Department of Energy) for sponsoring this research.

The invaluable help and support of Drs. Michael S. Story and Michael Weber-Grabau (Finnigan MAT, San Jose, CA) in designing and assembling the MINITMASS system is gratefully acknowledged. Dr. A. Peter Snyder (U.S. Army CRDEC, Aberdeen, MD) is thanked for his continued advice and participation in various phases of the project.

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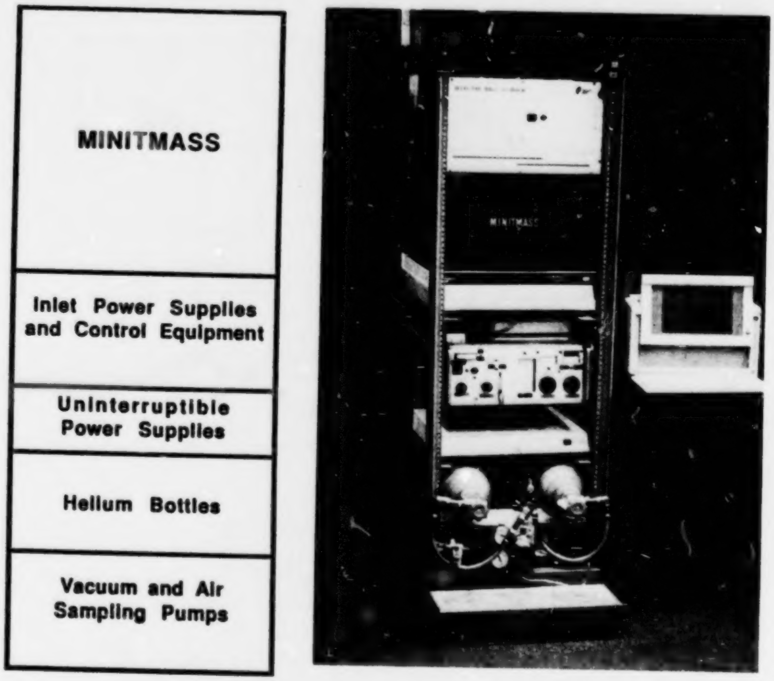
MINITMASS
Inlet Power Supplies and Control Equipment
Uninterruptible Power Supplies
Helium Bottles
Vacuum and Air Sampling Pumps

Figure 1. The MINITMASS system and associated equipment.

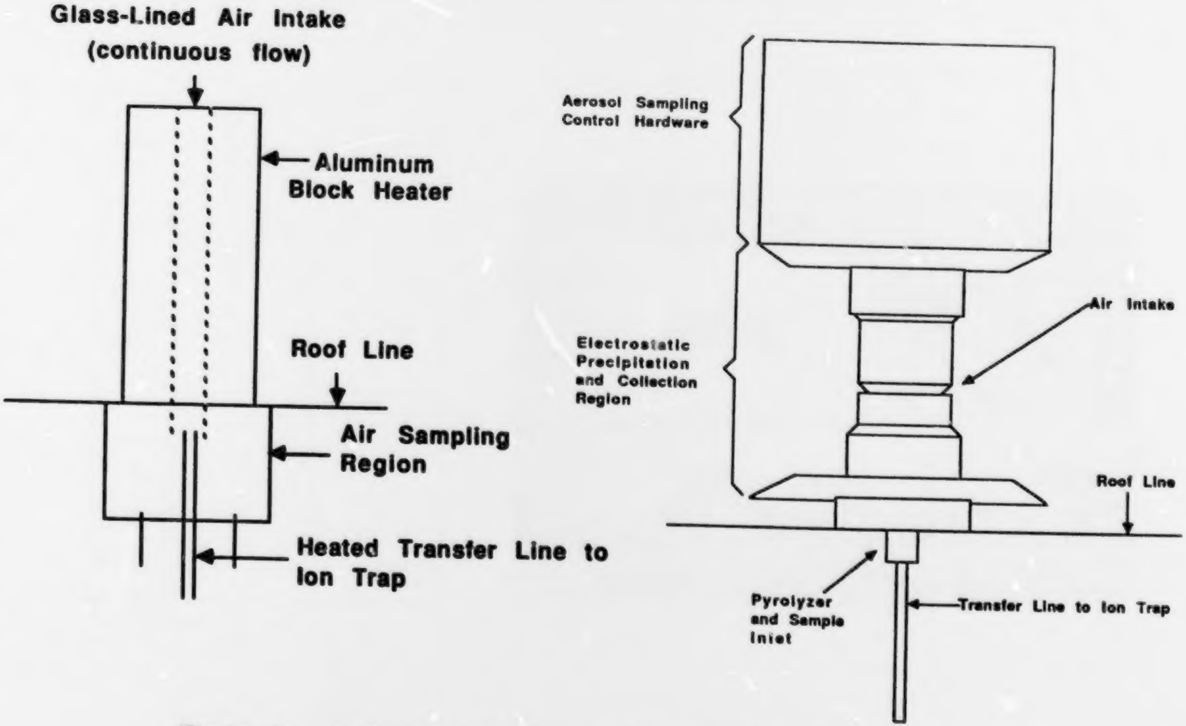
Glass-Lined Air Intake (continuous flow)
Aluminum Block Heater
Roof Line
Air Sampling Region
Heated Transfer Line to Ion Trap
Aerosol Sampling Control Hardware
Air Intake
Electrostatic Precipitation and Collection Region
Roof Line
Pyrolyzer and Sample Inlet
Transfer Line to Ion Trap

Figure 2. a) Highly schematized line drawing of the vapor sampling inlet; b) of the aerosol pyrolysis inlet.

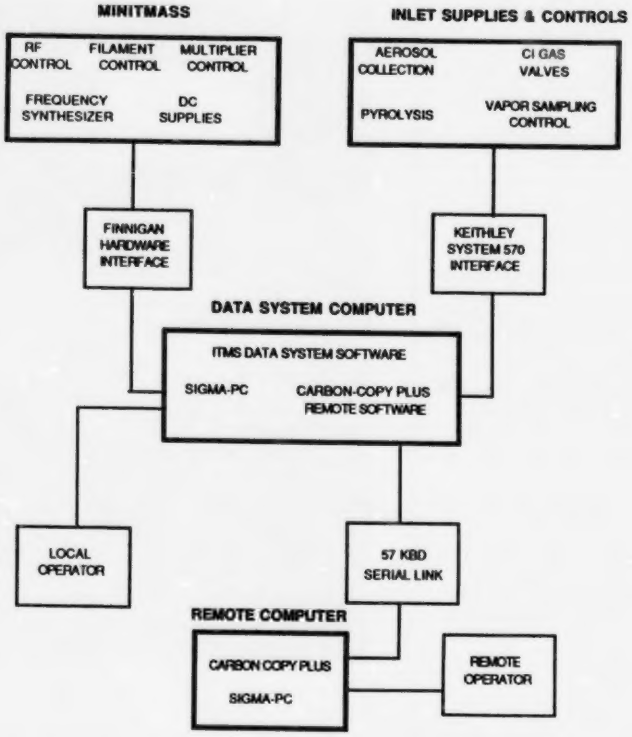
MINITMASS
RF CONTROL
FILAMENT CONTROL
MULTIPLIER CONTROL
FREQUENCY SYNTHESIZER
DC SUPPLIES
INLET SUPPLIES & CONTROLS
AEROSOL COLLECTION
CI GAS VALVES
PYROLYSIS
VAPOR SAMPLING CONTROL
FINNIGAN HARDWARE INTERFACE
KEITHLEY SYSTEM 570 INTERFACE
DATA SYSTEM COMPUTER
ITMS DATA SYSTEM SOFTWARE
SIGMA-PC
CARBON-COPY PLUS REMOTE SOFTWARE
LOCAL OPERATOR
57 KBD SERIAL LINK
REMOTE COMPUTER
CARBON COPY PLUS
SIGMA-PC
REMOTE OPERATOR

Figure 3. Block diagram of MINITMASS control system.

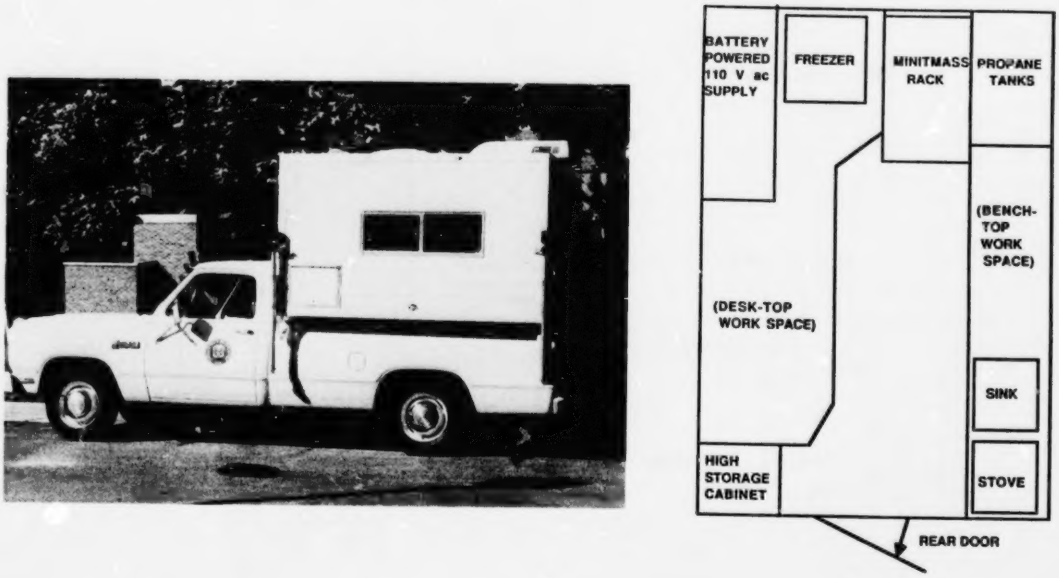
BATTERY POWERED 110 V ac SUPPLY
FREEZER
MINITMASS RACK
PROPANE TANKS
(BENCH-TOP WORK SPACE)
(DESK-TOP WORK SPACE)
SINK
HIGH STORAGE CABINET
STOVE
REAR DOOR

Figure 4. Mobile laboratory module

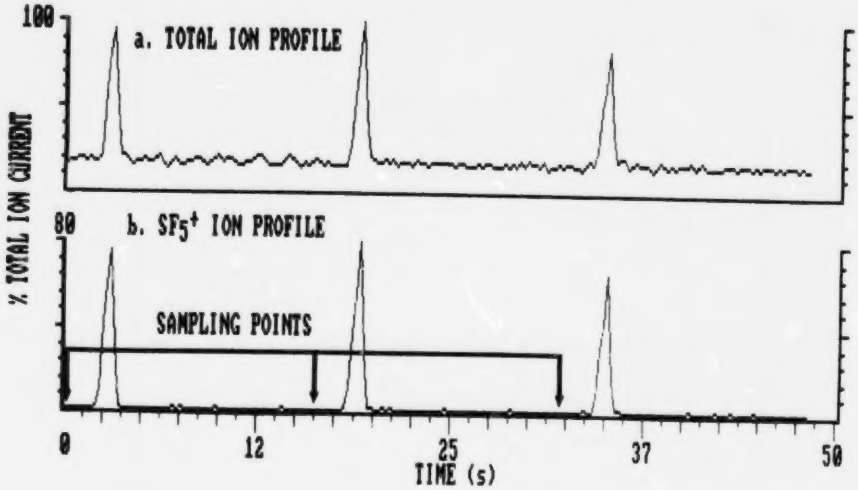

Figure 5. Repetitive vapor sampling of approx. 40ppm SF_6 in air showing a) the total ion chromatogram and b) the SF_5^+ ion chromatogram. Samples were taken for 2 s at 16 s intervals with EI-MS analysis for that main fragment ion SF_5^+ at m/z 127.

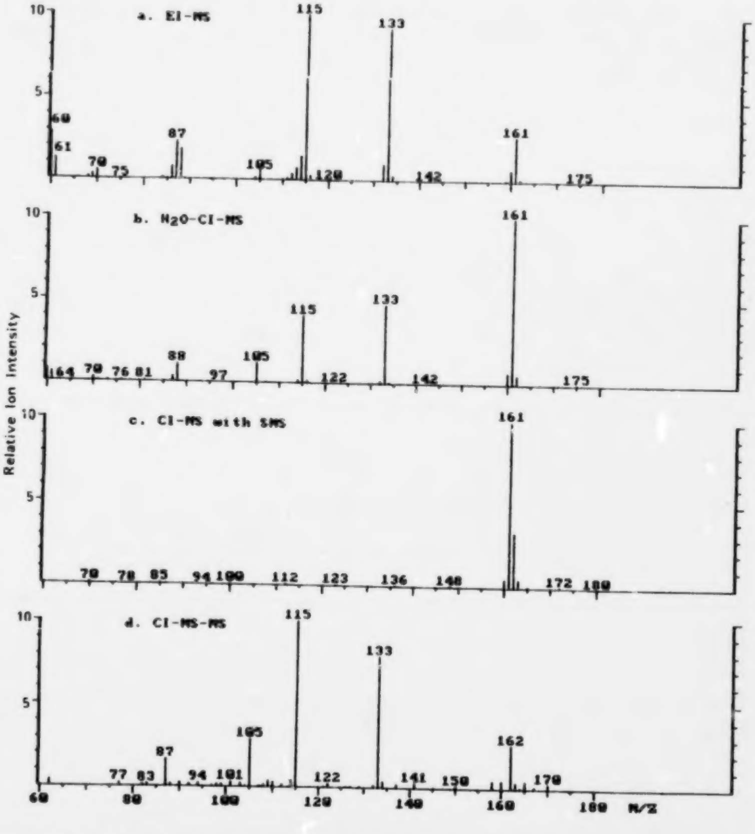

Figure 6. Diethyl malonate (DEM) mass spectra using a) electron ionization (EI), b) water chemical ionization (H2O-CI, c) CI-MS with Selective Mass Storage (SMS), and d) CI tandem MS (MS/MS). The protonated molecular ion (M+H)+ occurs at m/z 161 and is isolated using SMS prior to collision-induced dissociation to maximize both sensitivity and selectivity.

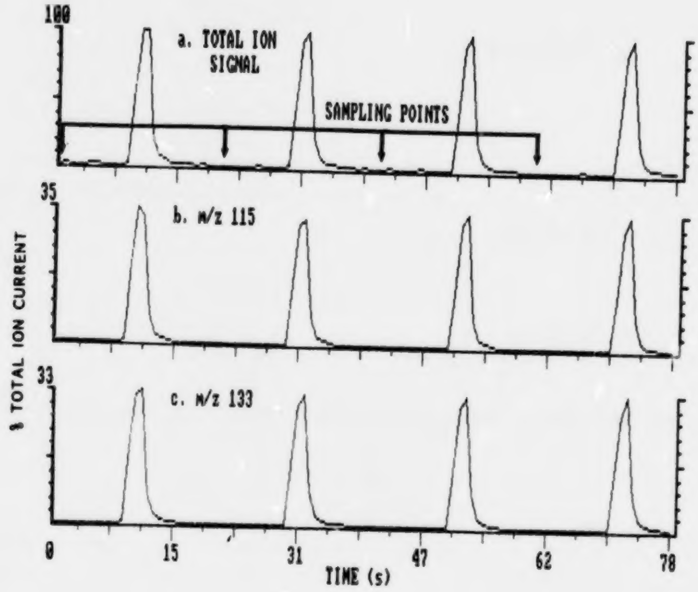

Figure 7. Repetitive analysis of DEM vapors in air using H_2O-CI-MS/MS (see Figure 6d). Data is represented by chromatograms for a) the total of all ions from m/z 50 to 200, b) DEM fragment ion at m/z 115, and c) DEM fragment ion at m/z 133. The 3 s samples were taken at 20 s intervals at the points indicated.

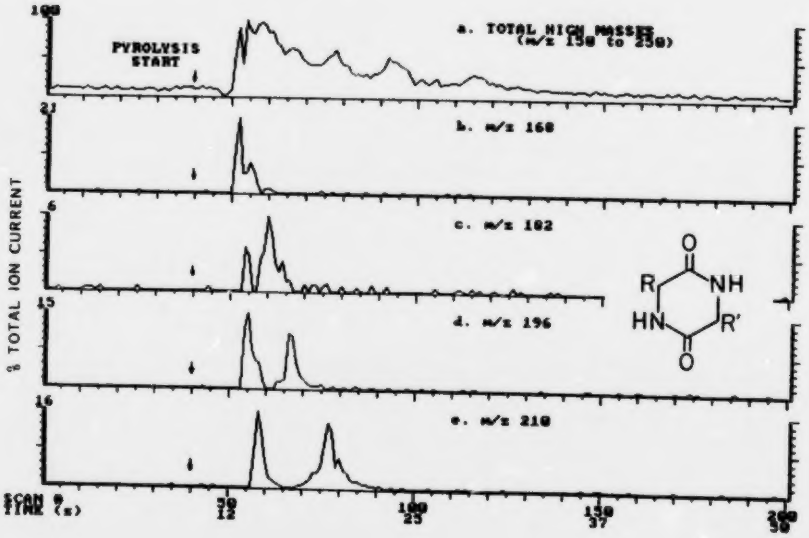

Figure 8. Pyrolysis TLGC-CI-MS analysis of bovine serum albumin (BSA) aerosol collected by electrostatic precipitation. Ion profile chromatograms are shown for the total of ions between m/z 150 to 250 (a) and single ion intensities at m/z 168 (b), m/z 182 (c), m/z 196 (d), and m/z 210 (e) tentatively identified as amino acid dimer ions of the general form shown.

DISCUSSION

TOM PRITCHETT: You said that basically you can do any type of chemical ionization rather than having to just rely on ambient air?

HENK MEUZELAAR: Yes, you could do ammonia, isobutane, water chemical ionization. Others have played with other reagents.

TOM PRITCHETT: What about the inlet system?

HENK MEUZELAAR: The inlet does not limit the chemical ionization.

MARC WISE: We're also working with an ion trap mass spectrometer for environmental applications. Preliminary tests on samples in water and soil matrices indicate that we have very good detection limits at sub-part per billion levels, with very good linearity and quantitative reproducibility.

In real-life samples, do you have any problems with really unwanted ion molecule reactions at long chemical ionization reaction times?

HENK MEUZELAAR: Yes, when the sample amounts become high, then, especially in the electron ionization mode, you're likely to start seeing some chemical ionization and other types of high-pressure, long-residence time effects.

However, when you choose the chemical ionization mode, and the agent gas is the dominant reactant, then you can avoid those in most cases. It does require balancing, sometimes, of reaction times and total residence times. There is some experimental software that allows you to almost Macintosh-style program how the trap will scan, how long you will react. The problems that you mention exist, but I think they can be overcome.

MARC WISE: For real-life samples where you're looking at a complex mixture, it's desirable, of course, to have an automated software program for parent ion scanning, particularly for tandem mass spectrometry. Have you developed any type of software for that? I think it can be done probably fairly easily.

HENK MEUZELAAR: No we haven't.

THE PREPARATION, CERTIFICATION, AND USE OF SUMMA CANISTER EXTERNAL PERFORMANCE EVALUATION SAMPLES IN SUPPORT OF THE TAGA 6000E INDOOR AIR ANALYSES DURING THE LOVE CANAL EMERGENCY DECLARATION AREA HABITABILITY STUDY

K. J. Caviston, Richard E. Means, Rita M. Harrel, B.J. Carpenter
Northrop Services, Inc.
David Mickunas & Mark Bernick
Roy F. Weston, Inc (REAC)
Thomas H. Pritchett
U.S. EPA Environmental Response Team

Because of the past problems encountered with the TAGA 6000E in quantitative air analyses and because of the high scrutiny that the Love Canal Emergency Declaration Area (EDA) air data would ultimately undergo, it became necessary to develop the procedures to provide external audit and performance evaluation (PE) samples to the TAGA during the study. Northrop Services, through the Quality Assurance Branch of EMSL/RTP, was requested by U.S. EPA Region II to provide this support. Northrop Services worked in conjunction with the Environmental Response Team (ERT) and its contractor to develop this support capability. The ERT and REAC, its contractor, first defined the procedures to be used to analyze the samples and then Northrop Services developed the procedures to prepare and certify the PE samples at the applicable concentrations. Both 16 Liter and 6 Liter Summa canisters were utilized during the study. Problems were initially encountered with sample stability in dry balance gas and with the certification analyses. These problems were solved. The 16 Liter canisters were successively used during all four phases of the EDA study and the 6 Liter canisters were successively utilized during the last two phases. These results will be summarized.

DISCUSSION

TOM PRITCHETT: One of the problems with doing any type of air or soil gas analysis, is that it is very difficult to get performance evaluation samples/standards that you can spike into bags or air samples. We have taken this procedure, and we are now – in conjunction with Northrop Services within the EPA – utilizing it for just about all our air analysis and soil gas analyses.

As a matter of fact, there is a directive coming out from the Environmental Response Division of OSWER that will require these types of performance evaluation samples to be used in soil gas and air sampling.

Basically, you can make up a mixture in a Summa canister, take it out in the field, spike it into your bag, send it back to the lab; or you can spike it onto a tube and send the tube back. This is just now coming on board, and it has a lot of potential beside the TAGA application described here.

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UNAMBIGUOUS IDENTIFICATION AND RAPID QUANTITATION IN FIELD AIR MONITORING USING A FULLY MOBILE MASS SPECTROMETER

Frank H. Laukien, Ph. D. and Thomas M. Trainor, Ph. D.
Bruker Instruments, Inc.
Manning Park
Billerica, Massachusetts 01821

ABSTRACT

A fully mobile field mass spectrometer, based on electron-impact ionization and medium-resolution quadrupole mass analysis, has been found to be useful for the detection and quantitation of volatile organics associated with hazardous waste site emissions or toxic emergencies. Ambient air monitoring may take place on a continuous basis in real-time and with excellent sensitivity, accuracy, and reproducibility, using an air sampler interfaced to the ion source of the mass spectrometer. Alternatively, time-integrated measurements may be made by concentrating whole air on a suitable sorbent tube for subsequent thermal desorption/high resolution gas chromatography-mass spectrometry analysis in the field.

INTRODUCTION

The detection of organic compounds in air remains a challenging analytical problem for the environmental community today. The frequency and type of operations surrounding hazardous waste site investigation and remediation activities, coupled with the variable wind velocity and direction normally encountered, invariably lead to unpredictable and intermittent excursions above background concentration levels for toxic compounds. During toxic emergencies, such as storage tank leaks or chemical transport accidents, immediate results are mandated. Many sampling and analysis approaches have been proposed for air monitoring of toxic organics associated with hazardous waste sites, with the currently most popular including direct (whole air) field-based measurements with gas chromatographs (1) or off-site laboratory analysis of samples collected in specially treated steel canisters (2), Tedlar bags (3), or pre-concentrated on suitable sorbent tubes (4). However, each of these approaches has inherent limitations which act to preclude universal applicability to investigations surrounding site emissions. For instance, the limited specificity afforded by field GC's has been a concern in many programs. Besides the data turnaround and logistic problems, researchers are increasingly noting the technical problems involved in off-site analysis, which include sample quality degradation caused by the combined sampling/transport/storage series of steps. The use of polished stainless steel canisters has been found to minimize these problems, but is recognized as introducing new concerns, including the cost of individual samplers (ca. $ 500 each) and problems concerning normal sample levels of water in subsequent cryotrapping GC and/or GC-MS analysis (2).

The use of field instrumentation is recognized as invaluable in adequately addressing the variable nature of airborne emissions. Atmospheric pressure ionization mass spectrometry has been suggested (API-MS) (5) as a means of conducting both the sampling and analysis directly in the field. However, deploying API-MS, particularly tandem GC/MS/MS, in the field represents the expense of an initial capital investment and highly trained staff of mass spectrometrists that few organizations can justify. Moreover, the complex, and often irreproducible (6), ionization behavior inherent in API-MS is in practice an impediment to routine problem-solving.

One technique that has been found to obviate the majority of these limitations is based on the development of a fieldable GC-MS which employs traditional electron-impact (EI) ionization. The Bruker Mobile Environmental Monitor has been designed to sample, identify, and quantitate target organic compounds in ambient air. The advantages realized by utilizing this mobile instrument include :

1. Direct sampling and analysis of whole air on a truly continuous real-time basis.
2. Generation of unambiguous electron-impact data, with the capability of both full-scan or selected ion monitoring (SIM) data acquisition.
3. Single keystroke operation, designed for non-expert operators.
4. Capable of operation with 24 volt rechargeable battery power under extremes of temperature, humidity, mechanical and electrical shock, without a need for compressed gas cylinders.

This presentation will cover the present range of applications and limitations of the Bruker MEM in air monitoring programs. Examples of both continuous and time-averaged sampling approaches will be discussed and actual results presented.

INSTRUMENTATION

The results reported here were carried out with standard Bruker MEM mobile mass spectrometers equipped with both the direct air/surface sampler and the optional thermal desorption-capillary gas chromatograph option. MEM control and data acquisition was carried out by either the internal MEM controller or the optional external data system (Compaq Portable III). The MEM, based on an electron-impact source and quadrupole analyzer, is described in detail in a separate paper at this symposium which should be consulted for general

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information and specifications (7). The data gathered here was obtained with MEM units mounted in a variety of vehicles, including a 4-wheel drive Chevy Blazer truck. Instrument power was provided by four 6-volt storage batteries connected in series. Gas standards were prepared using a Thermo Electron model 360 standards generator, or alternatively, by spiking known amounts of materials into Tedlar bags filled with UHP nitrogen. Tenax tubes were obtained from SKC and used as received. The fused-silica capillary GC columns employed included a 30 m x 0.32 mm DB-624 for the auxiliary capillary GC oven, and a 3.5 m x 0.32 mm SE-54 for the direct air/surface sampler.

CONTINUOUS AIR MONITORING BY SELECTED ION MONITORING GC-MS

The simplest approach to continuous air monitoring with the MEM is by means of sampling with the air/surface sampler (7) while acquiring data using the program AIR MONITOR. AIR MONITOR allows for the continuous acquisition and display of selected ion monitoring data for up to a maximum of 22 compounds simultaneously, using from 1 to 4 selected ions per compound. An individual METHOD file, of which a maximum of 15 may be permanently stored in the MEM EE-prom memory, may contain a preprogrammed library of up to 60 target compounds, thus allowing for a total of 900 unique compounds stored in memory. An example of a SUBSTANCE DATA page from a typical method is shown in Figure 1. Here, four characteristic ions with the corresponding per cent relative intensities are entered, along with the compound name and numerical values for five additional parameters.

During actual air monitoring, a real time display of MEM response, on a logarithmic basis, is shown on the video screen, Figure 2. Target compound ion groups are labeled A - L along the x-axis, while the corresponding ion abundances are plotted along the y-axis. A constant measurement of the high vacuum region's pressure is also displayed along the right-hand edge of the screen. Prior to initiating an AIR MONITOR experiment, the MEM conducts a background measurement by scanning each ion five times which permits the calculation of a value known as the Minimum Detection Amount (MDA) for each ion. This MDA is defined as 3 times the square root of the mean ion response observed during the background measurement. This MDA is graphically represented throughout the subsequent AIR MONITORING run by the unshaded area under the curve drawn for each designated compound (Figure 2).

The MEM has been programmed to determine in real-time both the qualitative identification and quantitation of target compounds based on the SIM results. During each acquisition cycle, the first ion of each compound is scanned and the observed background corrected signal is compared to the WARNING LEVEL value programmed for the corresponding compound (Figure 1). If the intensity of the first ion (I1) is greater than this WARNING LEVEL, then the three secondary ion signals are recorded (I2, I3, and I4). Figure 3 displays a flow chart illustrating the decision pathway that is followed by the MEM software in carrying out an identification based on the actual measured ion currents. The parameter RELIABILITY is a numerical value which governs the allowable variance between the library ion abundance ratios and the observed ratios (spectra matching criteria). INTERFERENCE is a parameter that functions to suppress false positive identifications as a result of signals from interfering compounds present in much larger concentrations relative to the target compound.

During the AIR MONITOR acquisition, the video screen is constantly updated in terms of the ion response information. Ion current significantly above background levels is depicted as the shaded areas directly above the MDA unshaded areas. As a further visualization aid to the operator, prior to the display update the observed signals of the secondary ions (I2, I3, I4) are ratioed to the expected relative abundance per cent values contained in the method library, and this normalized value is actually plotted. By carrying out this transformation, the end result is that for good library matches the ion peak heights will be near equal, leading to readily discernible "flat-topped" signal envelopes (Figure 3). Clearly, in instances where unequal ion peak heights above background are frequently observed, the operator immediately knows that non-target compounds are present, which may suggest taking a full mass spectrum to characterize the air components, and perhaps, making changes to the current list of compounds analyzed by AIR MONITOR.

Once an identification has been made in AIR MONITOR and a compound signal exceeds the preselected ALARM LEVEL, the compound name and maximum signal amount is displayed on the screen. If the instrument has been previously calibrated for the compound using gas standards of known concentrations, then a direct conversion to actual air concentrations (ppb or ppm) is made. Alternatively, for those compounds in which no instrument response factor is currently in memory, the raw log signal value is displayed. Figure 4 contains a typical calibration curve exhibited by the MEM for a series of benzene standards in which accurate readings in the range of 1 to 10 ppm were of interest for a particular application.

An extensive and thorough evaluation of the MEM for direct air sampling was recently reported by the US EPA Region II Environmental Response Team (ERT) (8). Under actual field conditions, using a variety of common volatile organic pollutants delivered as mixtures from certified gas cylinders, detection limits in the range of 10 to 100 ppb were found to be readily achievable. Linearity data was reported over the range of 10 ppb to 10 ppm for several compounds using the direct air/surface sampler. The instrument stability over time was such that quantitation error levels fell in the range of +2.2% to -39.1% for a series of test analytes introduced at the 100-600 ppb range.

AIR MONITORING BY THERMAL DESORPTION GC-MS

Frequently, for highly complex air matrices in which many interferences exist at the ions monitored for the actual target compounds of interest and/or instances where the detection limits achievable with the direct air/surface sampler are not adequate, we have found the optional MEM capillary GC to be of benefit. The improved chromatographic resolving power of the 30 m capillary column is particularly suited to multi-component mixtures. The thermal-desorption injection system incorporated in the GC allows for the direct analysis of air samples concentrated on glass tubes containing suitable sorbent materials. An example of this approach was an analysis developed on the MEM for the suspected carcinogen bis-dichloromethyl ether (BCME) in air associated with a manufacturing facility. Due to the high levels of interferences from other volatile organics present at the site, and the need for sub-ppb detection limits, initial concentration on Tenax followed by thermal-desorption capillary GC-MS was utilized. Typical results are shown here for a calibration curve (Figure 5) and a 1.0 ppb BCME standard run (Figure 6) achieved using Tedlar bags for the preparation and delivery of suitable calibration standards to the Tenax traps. Under the AIR MONITORING data acquisition conditions, this level of BCME resulted in a signal approximately 10x the background level.

For many programs the generation of full-scan electron-impact data on capillary GC separations is necessary. With the optional MEM external data system (Compaq Portable III) this high-speed, memory intensive activity is possible in the field. An application of this is depicted by the MEM chromatogram shown in Figure 7. Here, sampling via Tenax of a site suspected of hydrocarbon contamination was of interest. By careful examination of several samples taken both upwind and downwind of the site, during remediation activities carried out under highly variable wind conditions, potential off-site impacts were determined and appropriate precautions taken immediately.

CONCLUSIONS

A gas chromatograph-mass spectrometer uniquely designed for operation in the field has been shown to provide solutions to analytical problems associated with the ambient air monitoring of organic compounds.

ACKNOWLEDGMENTS

Assistance provided by Dr. Jochen Franzen and Dr. Alex Loudon, of Bruker-Franzen Analytik Gmbh, is greatly appreciated.

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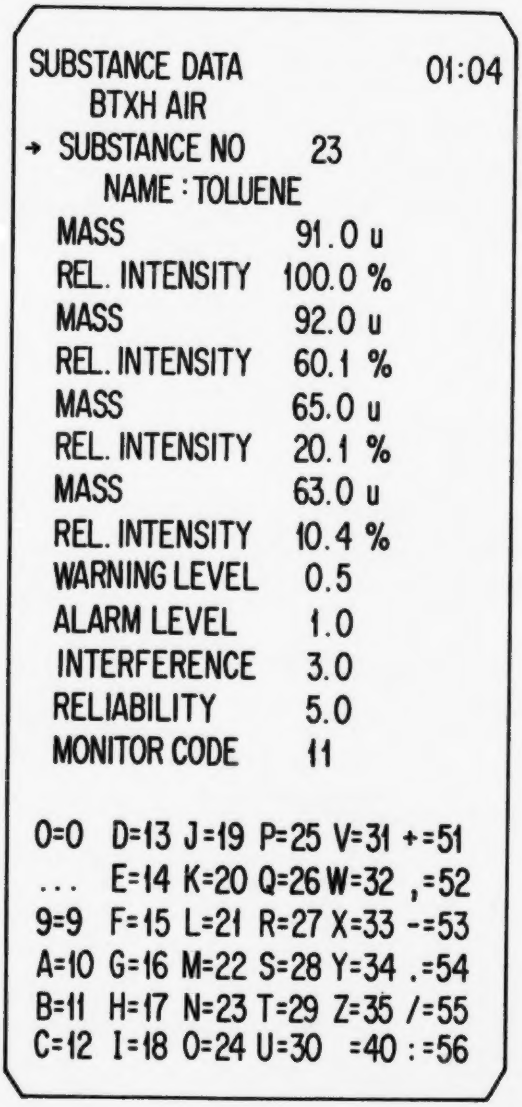

```
SUBSTANCE DATA                01:04
    BTXH AIR
→ SUBSTANCE NO       23
     NAME : TOLUENE
  MASS               91.0 u
  REL. INTENSITY    100.0 %
  MASS               92.0 u
  REL. INTENSITY     60.1 %
  MASS               65.0 u
  REL. INTENSITY     20.1 %
  MASS               63.0 u
  REL. INTENSITY     10.4 %
  WARNING LEVEL       0.5
  ALARM LEVEL         1.0
  INTERFERENCE        3.0
  RELIABILITY         5.0
  MONITOR CODE        11

 0=0  D=13 J=19 P=25 V=31 +=51
 ...  E=14 K=20 Q=26 W=32 ,=52
 9=9  F=15 L=21 R=27 X=33 -=53
 A=10 G=16 M=22 S=28 Y=34 .=54
 B=11 H=17 N=23 T=29 Z=35 /=55
 C=12 I=18 O=24 U=30   =40 :=56
```

FIGURE 1. EXAMPLE SUBSTANCE DATA PAGE FOR A TARGET COMPOUND (TOLUENE) STORED IN AN MEM AIR MONITOR METHOD FILE.

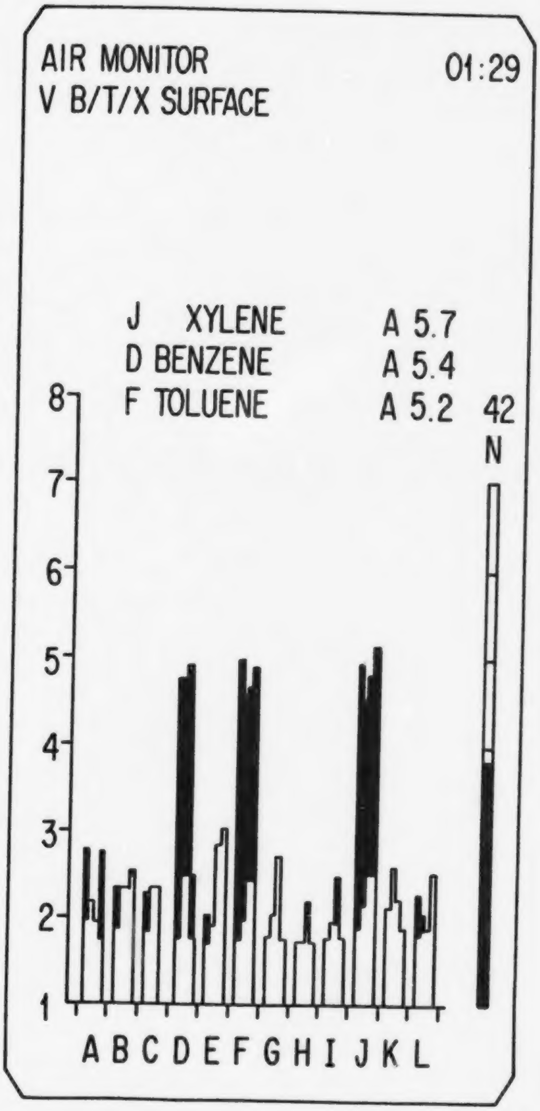

FIGURE 2. EXAMPLE OF THE MEM AIR MONITOR REAL-TIME VIDEO DISPLAY.

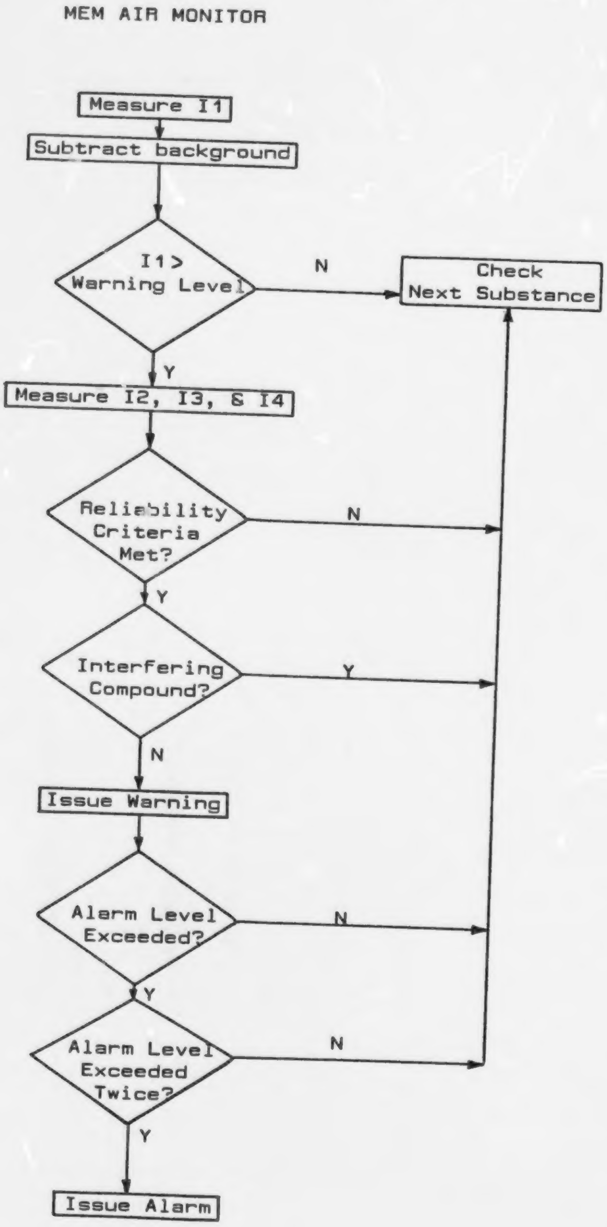
MEM AIR MONITOR
Measure I1
Subtract background
I1 > Warning Level
N
Check Next Substance
Y
Measure I2, I3, & I4
Reliability Criteria Met?
N
Y
Interfering Compound?
Y
N
Issue Warning
Alarm Level Exceeded?
N
Y
Alarm Level Exceeded Twice?
N
Y
Issue Alarm

FIGURE 3. FLOW CHART DESCRIBING THE MEM AIR MONITOR PROGRAM.

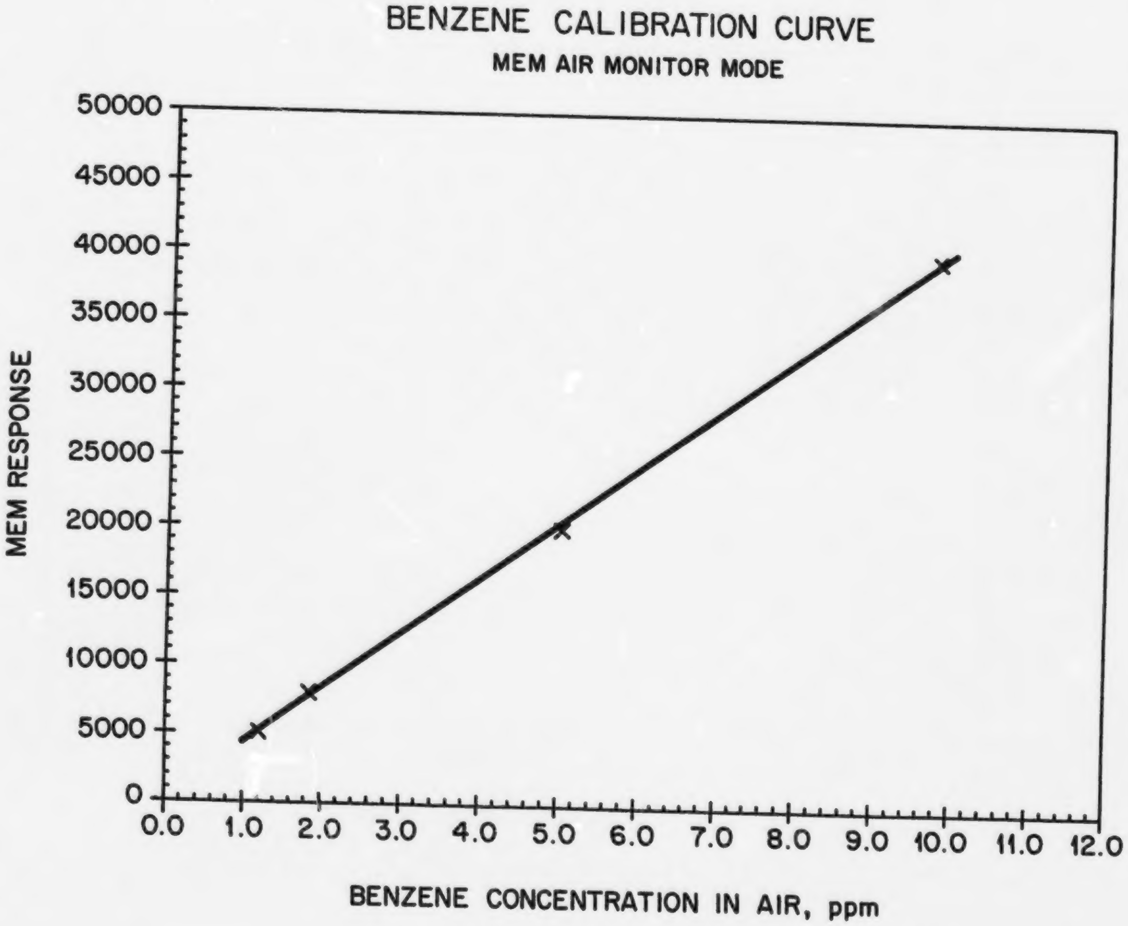

FIGURE 4. CALIBRATION CURVE FOR THE DETERMINATION OF BENZENE USING AIR MONITOR.

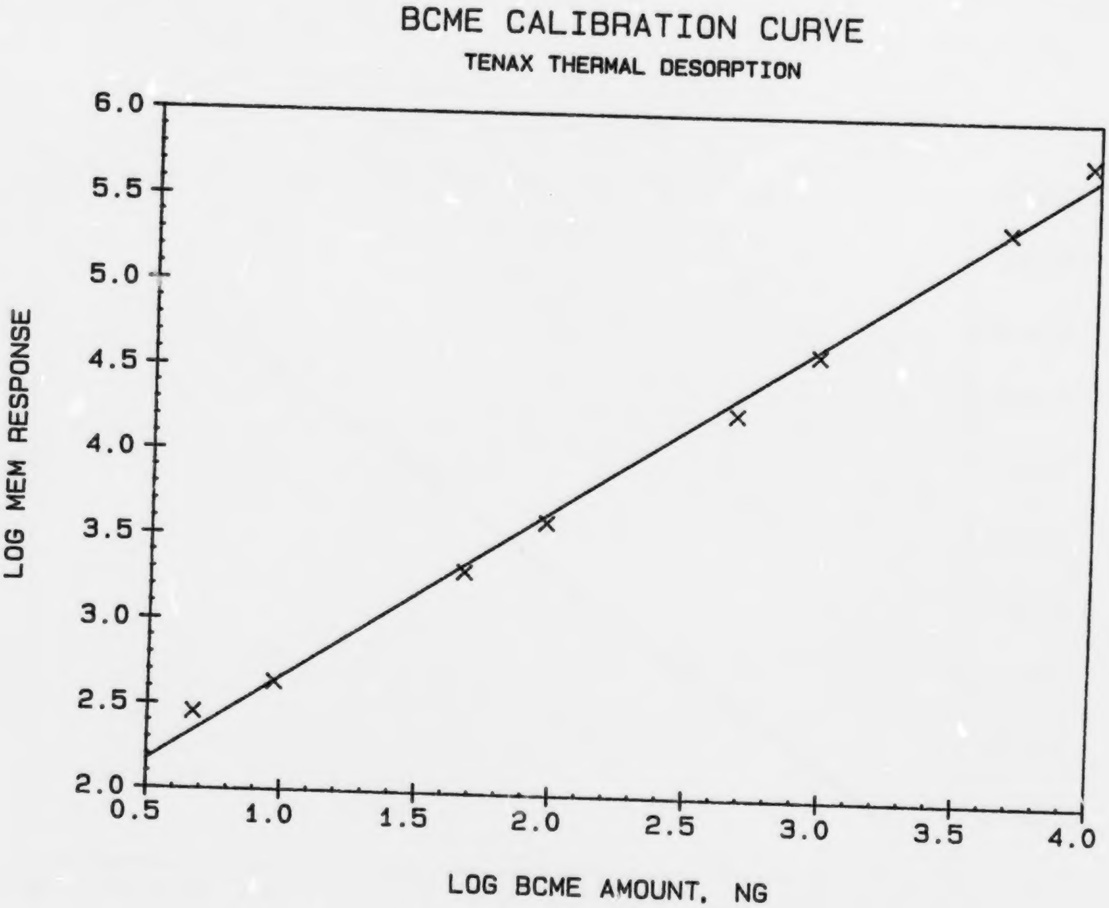

FIGURE 5. CALIBRATION CURVE FOR BCME ISOLATED ON TENAX.

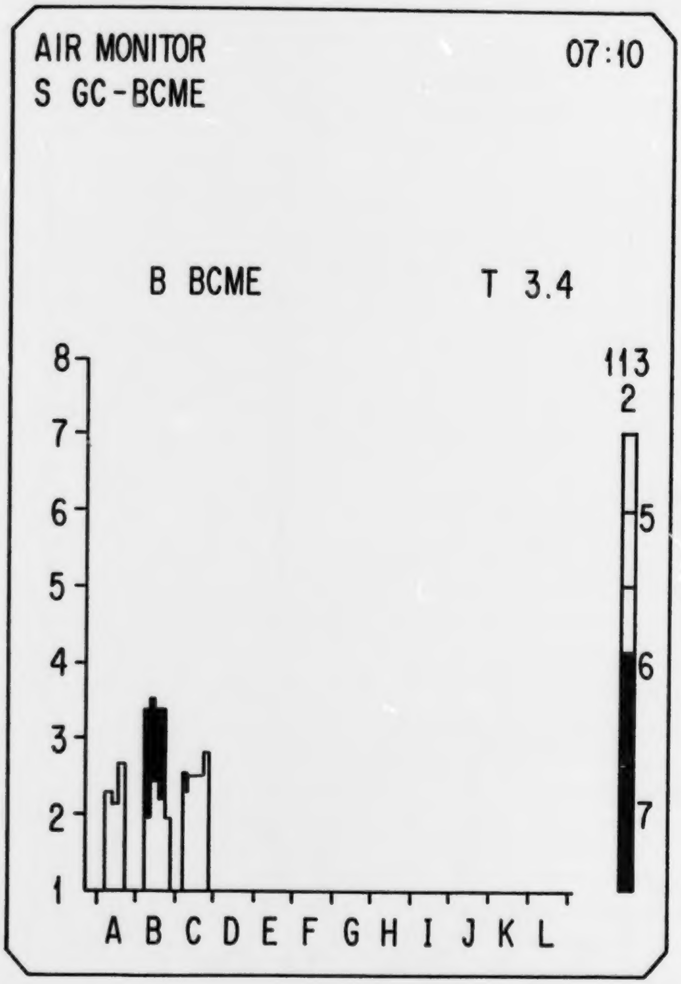

FIGURE 6. AIR MONITOR RESPONSE FOR 1.0 PPB BCME (10 1 AIR SAMPLE).

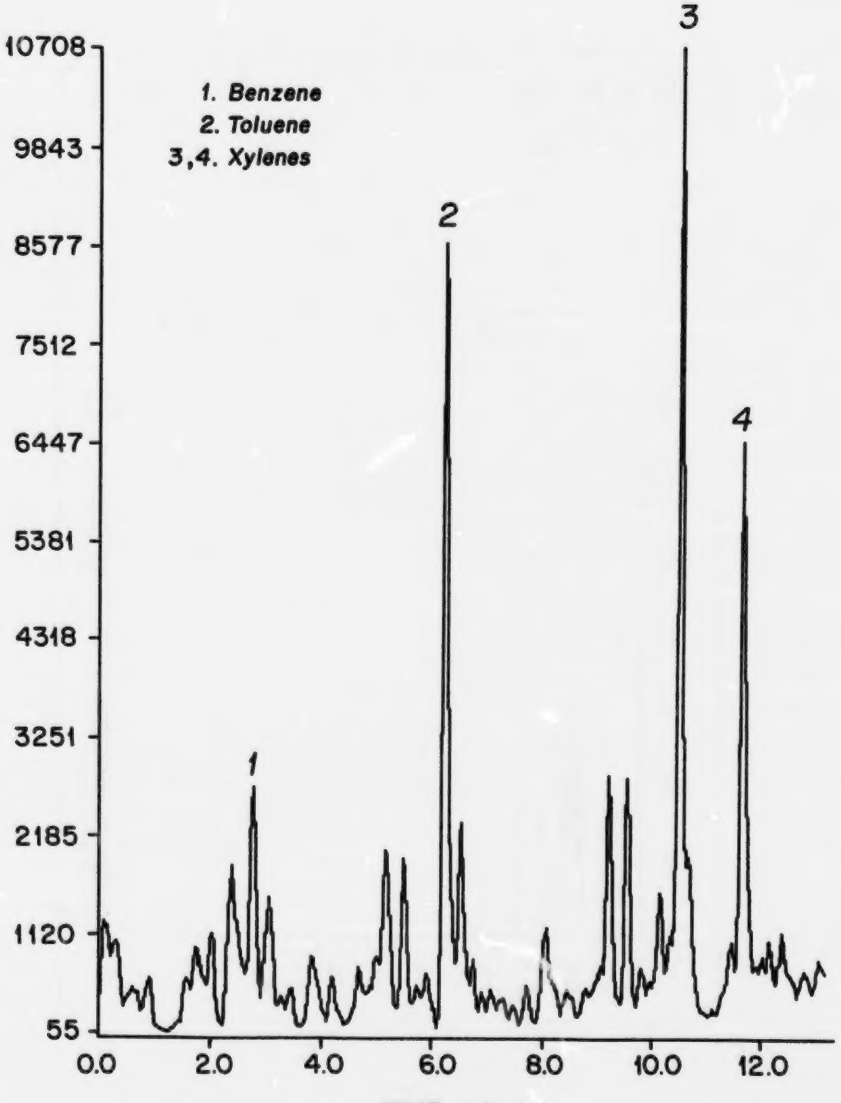

FIGURE 7. TOTAL ION CURRENT PROFILE FROM THE THERMAL DESORPTION GC-MS ANALYSIS OF A TENAX FIELD SAMPLE.

DISCUSSION

TOM PRITCHETT: What absorbents have you looked at on your GC? Have you evaluated different absorbents?

FRANK LAUKIEN: We have not really done very scientific studies. We have looked at 10 or 15 different absorbents. We use either Tenax, or most of the time for the VOCs, we use two-thirds charcoal and one-third Tenax to prevent breakthrough of the very volatile chemicals. We have relied on others' experiences.

DON FLORY: I've seen a lot of advantages listed here for taking instruments out into the field, especially in terms of turnaround time for results. But we should note that we're dedicating these instruments to this project when we take them out into the field. And if we dedicate the lab instruments to the project in the same manner, we'd get about the same turnaround time.

FRANK LAUKIEN: In the field applications, getting the final report takes just as long as it does to get a final report out of lab. But when you're in the field making a decision the next morning, there is no way that you can get any results from any laboratory in less than 48 hours. I have been out in the field with field analytical equipment where samples came in at 3:00 in the afternoon and by 7:00 the next morning they needed to know what dirt to move, or someones begins wasting about $6,000 a day. There's just no way you can meet that schedule with a fixed lab. When a site gets out of control, something unexpected has happened. That's the advantage of a field analytical lab over a fixed lab.

THE PREPARATION OF SUMMA CANISTER PERFORMANCE SAMPLES AND THEIR SUBSEQUENT ANALYSIS BY THE TAGA 6000E MS/MS

Rita M. Harrell, Richard E. Means, and Kenneth J. Caviston
NSI Technology Services Corporation
P.O. Box 12313
Research Triangle Park, NC 27709

Mark Bernick and David Mickunas
Roy F. Weston, Inc. (REAC)
GSA Raritan Depot
Edison, NJ 08837

Thomas H. Pritchett
US EPA Environmental Response Team
GSA Raritan Depot
Edison, NJ 08837

William J. Mitchell, PhD
U.S. EPA Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27711

ABSTRACT

For the indoor air portion of the Love Canal Emergency Declaration Area Habitability Study, summa canister performance evaluation samples were prepared and certified by NSI according to specifications defined by the U.S. EPA Environmental Response Team. These samples were then analyzed in the field by the TAGA 6000E MS/MS using procedures developed by the ERT and Roy F. Weston. Preparation and analysis procedures are discussed along with various problems which had to be overcome initially. TAGA results for these canisters are then presented along with deviations from expected results. Finally, these results are compared to the data quality objectives of the study.

INTRODUCTION

NSI was directed[1] by the Quality Assurance Division of EPA/EMSL/RTP to provide QA support to EPA's Love Canal Emergency Declaration Area Habitability Study at Niagara Falls, NY.

A major portion of this support was the preparation of blind 6L and 16L summa canisters containing the two selected Love Canal Indicator Chemicals (LCIC's) chlorobenzene and chlorotoluene. These canisters, prepared at the 20-50 PPM level, were used to check the performance of the TAGA 6000E MS/MS instrument being used in the study.

This report describes the procedures used to clean the canisters prior to sample preparation, preparation, NSI analysis by GC/FID, the TAGA analysis results, and comparison of the TAGA results with the QA objectives outlined in the study's Quality Assurance Project Plan (QAPP).

EXPERIMENTAL

Canister Cleaning

Figure 1 shows a schematic drawing of the canister cleaning apparatus used. It consists of a vacuum pump, a 1/4 " coiled copper tubing trap, a Dewar flask for liquid N2, a thermocouple vacuum gauge with a range of 1-1000

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µm of Hg, a bubble flowmeter, an oven suitable for heating 2 6L canisters simultaneously, 1 3-way valve, 3 2-way valves, and copper connective tubing.

Prior to canister cleaning, the copper coil is cleaned to remove contaiminants and H2O. With valves B and D open, the coil is purged for about 10 min with high purity N2 while being heated with a heat gun. After the coil has cooled, valves B and D are closed, the Dewar is replaced and carefully filled. The vacuum pump is then turned on. Valve A is opened and after a few minutes valve C is opened. When the vacuum gauge indicates a vaccum of 10 µm, the 3-way valve, D, is opened to the canisters. The canister valves remain closed until the gauge again reads 10 µm One of the canister valves is then opened and that canister evacuated to 500 µm It's valve is then closed while the other canister is evacuated to 500 µm. Both canisters are then opened to the vacuum system and while being heated at 75-85 °C evacuated to 10-25 µm. The evacuated canisters are then repressurized with humidified zero air and the cleaning process repeated.

In order to determine the efficiency of cleaning, the canisters are again pressurized with humidified zero air and 0.250-0.500L samples are cryogenically collected and analyzed by GC/FID under the same conditions used for analyzing standards. Under these conditions $\leq$ 0.5 PPB are detectable for most VOC's. For the Love Canal Habitability Study 25 % of the canisters were checked in this manner and reevacuated for use.

Canister Preparation

A volumetric procedure was used to prepare the two component mixtures used in the Love Canal Study. This procedure was selected because of it's simplicity and the time constraints involved for preparation, NBI analysis, and shipment to the field.

After calculating the amounts of neat chlorobenzene and chlorotoluene required for preparing 6L and/or 16L canisters in the desired concentration range, aliquots of pure compounds were transferred via Class S syringes to a small septum vial, where they were mixed thoroughly to form a master solution. Prior to introducing the master solution, the absolute pressure of each canister was checked using a absolute pressure gauge to insure that it was still under vacuum (see Figure 2). The canister valve was then closed and later reopened simultaneously with a fine metering valve in line between the canister and a cylinder of zero air. The flow rate of air was adjusted so as to maintain an absolute pressure of about 15 PSIA. Using a class S gas/liquid tight syringe, an aliquot of the master solution was removed from the vial and the liquid column drawn up into the syringe barrel for measurement. It was then injected into the flowing air stream at the septum fitting. After injection, any liquid remaining in the syringe was drawn into the barrel and measured, so that the actual volume of liquid injected was known. The absolute pressure at the time of injection was also noted. Mild heat was also applied in the injection area to facilitate sample evaporation. After 5-10 min the canister valve was opened fully and the desired final pressure reached in 20-30 min. The valve was then closed and the canister allowed to sit for about 1hr before taking a final pressure reading. This pressure was also noted and the theoretical PPM of chlorobenzene and chlorotoluene in the canister determined.

Calibration

Calibration curves were prepared using diffusion tubes (see Figure 3) containing chlorobenzene and p-chlorotoluene as the functioning elements of a diffusion chamber calibration system. Diffusion of material through the tube neck was predictable and was measured very precisely. By measuring weight loss over an extended period of time, during which the tube was being held at a constant temperature with a constant flow of N2 across the tube (see Figure 4), an accurately known quantity of the diffused material in the gas stream was obtained. This in turn developed a very precise primary standard which was traceable to NBS. Using basic diffusion theory the tube parameters, weight loss, and a programmable calculator the diffusion rate for each component was determined in ng/min.

The 3-5 point calibration curves were prepared by trapping chamber stream samples cryogenically while holding the flow rate to the trap constant and varying the trapping times, then analyzing them using a

Tracor 550 GC/FID. An OV-17 glass capillary column 50m x 0.5mm ID with a 2.5 µm film thickness was used. Addtional GC parameters were as follows:

Detector Temp.	250 °C
Column Flow	5cc/min
Make Up Gas Flow	30cc/min
Cryofocusing	manually 1min before end of trapping
Oven Program	ti=30 °C hold 1min manually close oven door 5 °C/min tf=130 °C

After all analyses had been completed, ng were determined and in this case converted to µg before plotting versus the corresponding peak areas. For the period of interest, chlorobenzene gave a linear response for µg versus area but chlorotoluene showed some scattering at higher concentration levels. However, on a curve to curve basis, it was found that 24 of 25 correlation coefficients for chlorobenzene were between 0.99 and 1.01 with 8 values of exactly 1.00. For p-chlorotoluene 15 of 16 values were between 0.99 and 1.01 and again 8 values were exactly 1.00. The curve that did not meet these criteria was excluded.

Canister Analysis

Using the same GC/FID conditions as for chamber analyses, 3-5 replicate 7.5 mL samples from each canister were analyzed and the µg of chlorobenzene and chlorotoluene determined for each sample. PPM were were calculated for the individual samples and the means of the acceptable values used for reporting overall canister concentration. Figure 5 illustrates a typical chromatogram with the appropriate µg and PPM.

RESULTS AND DISCUSSION

The QAPP for the Love Canal Habitability Study lists eight QA objectives two of which were TAGA 6000E accuracy and precision.

TAGA accuracy was to have been determined in all 4 phases of the study using blind canisters supplied by NSI. However, during the early stages of the study the canisters were not used as true performance evaluation samples because NSI analysis procedures were still in the development stage and a standard had not been set for acceptance or rejection of canisters. A major problem that NSI had to deal with in analyzing the canisters was the concentration level that was necessary so that the TAGA could efficiently analyze the field diluted samples. A gas dilution system was unavailable and in order to avoid overloading the GC column and detector a relatively small 7.5mL (5 cc/min, 1.5 min collection time) sample from the canister was analyzed. There were also problems with build up and/or hold up of the compounds in the lines and valves between the canisters and the cryogenic trapping system for the GC. These problems were compensated for by allowing the sample to purge through the entire system for a few minutes before sample collection and purging the system between canisters with zero air or helium for 2 hours with the GC oven at 200 °C. The purge stream was also analyzed before proceeding to another canister. Also, after each day's analyses, the system was purged overnight with the GC oven at 200 °C. Thus, during this development stage, the TAGA instrument accuracy was primarily measured using Scott standard cylinders of the type used for TAGA calibration. The analyzed cylinder was never the same cylinder which was used for the applicable calibration. Starting in phase 2 the 16L were used to determine the overall accuracy of the TAGA and in phases 3 and 4 both 6L and 16L canisters were used.

The accuracy QA objective for the TAGA was that the magnitude of error in its' analysis values be 25 % or less from the reference values. Relative accuracy as measured by the Scott cylinders never exceeded an absolute value of 25 % on any day during the four mobilizations. The largest magnitudes of the relative errors measured by this analysis were 23.1 % and 23.0 % for chlorobenzene and chlorotoluene, respectively. During phases 3 and 4, the relative error measured by the 6L canisters never exceeded an absolute value of 25 % for either compound. Overall, for all the 6L canisters analyzed by both NSI and the TAGA the 25 % limit was exceeded 3 times for chlorobenzene and 4 times for chlorotoluene. Investigation showed that the first two of these analyses had differences exceeding 25 % because of a problem in the TAGA delivery system which was later corrected. Table I summarizes NSI theoretical PPM chlorobenzene and chlorotoluene, NSI analysis values, TAGA analysis values, and the % differences from the theoretical values. The magnitude of the relative error for the compounds as measured by the 16L canister analyses only exceeded the 25 % criteria once for chlorotoluene during phases 2-4. However, on that day the magnitude of the relative errors for chlorotoluene as measured by the 6L canisters and the Scott cylinder were 8.8 % and 8.0 %, respectively. Figure 6 illustrates graphically the TAGA % differences from the theoretical concentrations when plotted in the order in which the canisters were analyzed. In general, chlorobenzene and chlorotoluene follow the same pattern showing a positive bias. Mean values of +1.7 for chlorobenzene and +2.5 for chlorotoluene confirm this. Figure 7 shows a similar plot for NSI analyses. For the most part NSI chlorobenzene results show a + bias and chlorotoluene compliments it with a - bias that is almost a mirror image. Using this data NSI means (8.8 for chlorobenzene and -8.4 for chlorotoluene) were determined and 2 x SD used to prepare a control chart for determining data acceptability. These values were 29.2 for chlorobenzene and 24.4 for chlorotoluene. Out of the 50 or so canisters prepared for the project only 3 did not meet this requirement and they were not used.

TAGA precision was determined by periodic cylinder/canister analyses. Again the criteria to be met was 25%. Day-to-day precision of the TAGA was actually determined from 2 sets of replicate analyses. First, as per the QAPP, the precision was determined from the daily analysis of the 16L summa polished canisters. The maximum relative standard deviations measured in these analyses throughout the study for chlorobenzene and chlorotoluene were 15.6 % and 17.9 %, respectively. Because of the larger number of analyses for each sample, the relative standard deviations were also calculated for Scott standard cylinder analyses. The maximum relative standard deviations measured in those analyses for chlorotoluene and chlorobenzene were 5.4 and 5.5, respectively. Both sets of data demonstrated that the TAGA analysis met the required data quality objective of 25 %.

In summary, it is clear that as a whole the TAGA 6000E MS/MS analyses met the Quality Assurance objectives for precision and accuracy. In those instances where this did not occur the problem was quickly located and corrected.

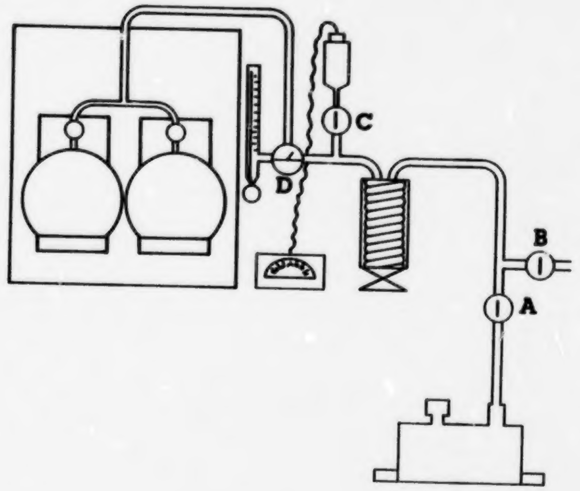
ACKNOWLEDGEMENTS

The authors would like to thank B.J. Carpenter, Shirley Henry, Annette King, and Karen Oliver at NSI Technology Services Corporation for their contributions to the study.

REFERENCES

(1). This support was provided under contract number 68-02-4444 with the U.S. EPA.

(2). Altshuller and Cohen, *Anal. Chem.*, 802, 1960.



Schematic of Canister Cleaning Apparatus

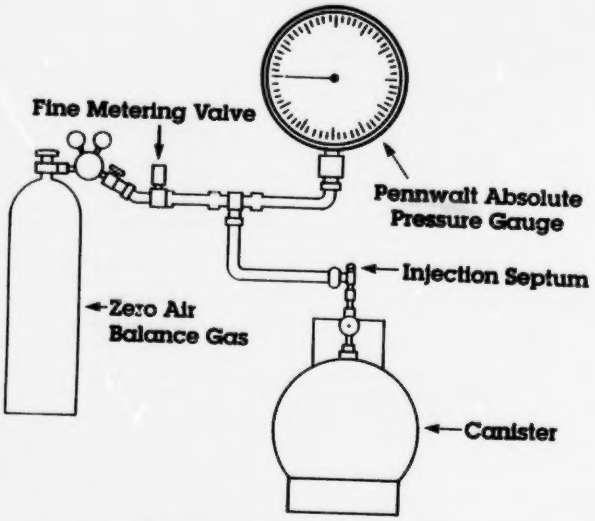

Fine Metering Valve
Pennwalt Absolute Pressure Gauge
Injection Septum
Zero Air Balance Gas
Canister

FIGURE 2. **Apparatus for Canister Preparation Using A Master Solution**

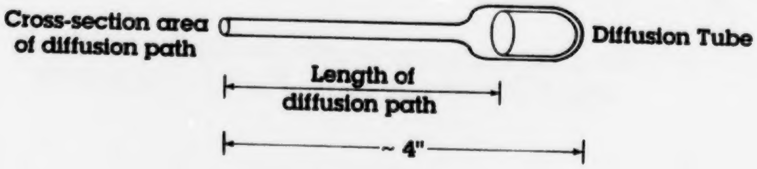

Cross-section area of diffusion path
Diffusion Tube
Length of diffusion path
~ 4"

FIGURE 3. DIFFUSION TUBE

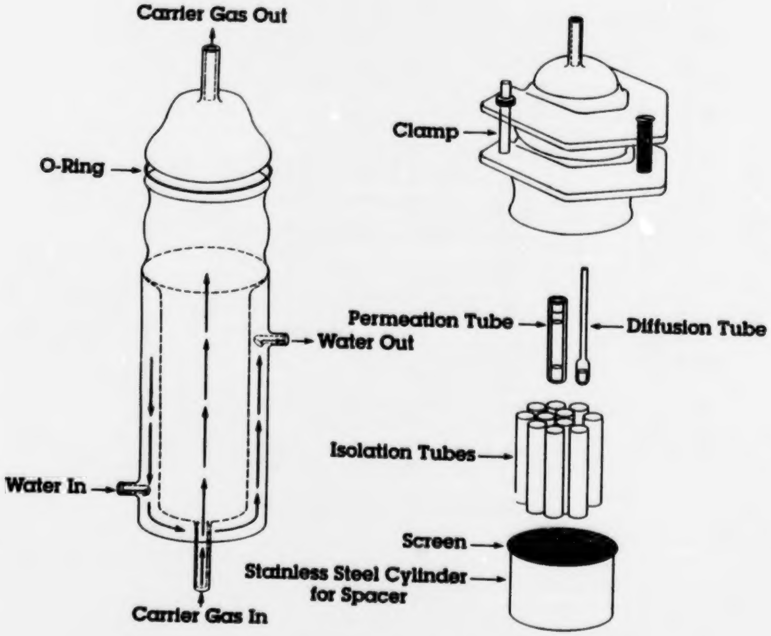
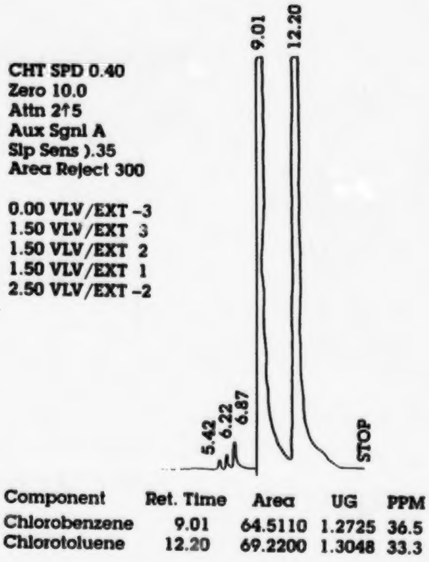

Carrier Gas Out
O-Ring
Water Out
Water In
Carrier Gas In
Clamp
Permeation Tube
Diffusion Tube
Isolation Tubes
Screen
Stainless Steel Cylinder for Spacer

FIGURE 4. DIFFUSION CHAMBER CALIBRATION SYSTEM



CHT SPD 0.40
Zero 10.0
Attn 2↑5
Aux Sgnl A
Slp Sens).35
Area Reject 300

0.00 VLV/EXT -3
1.50 VLV/EXT 3
1.50 VLV/EXT 2
1.50 VLV/EXT 1
2.50 VLV/EXT -2

Component	Ret. Time	Area	UG	PPM
Chlorobenzene	9.01	64.5110	1.2725	36.5
Chlorotoluene	12.20	69.2200	1.3048	33.3

FIGURE 5. **Sample Chromatogram for Chlorobenzene and Chlorotoluene on the Tracor 550 GC**

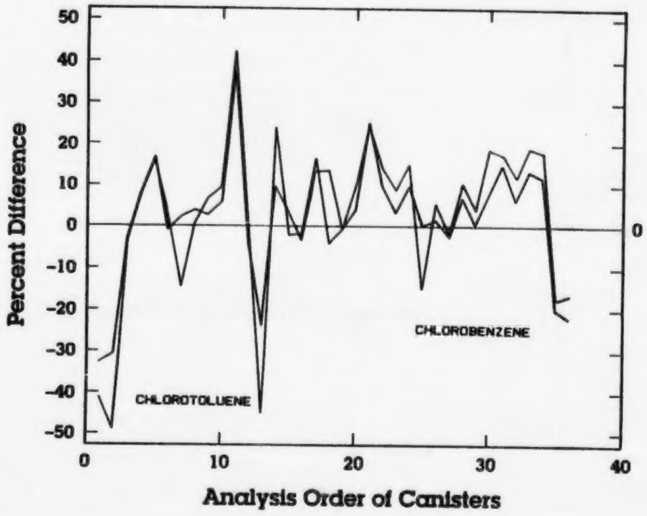


FIGURE 6. **TAGA Percent Difference by Analysis Order**

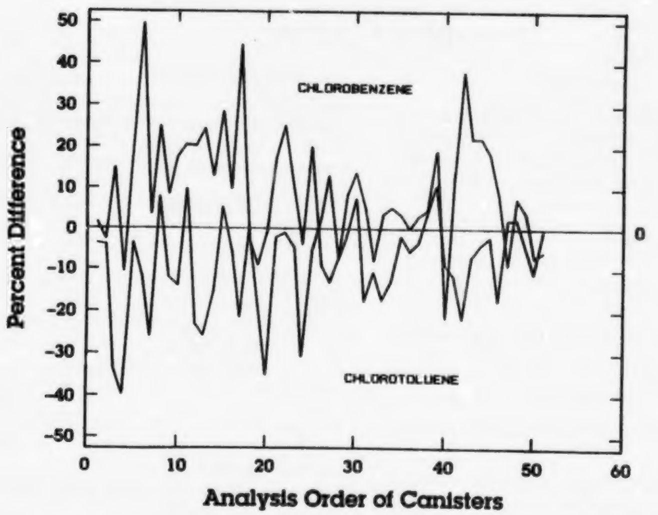


FIGURE 7. **NSI Percent Difference by Analysis Order**

TABLE I

CANISTER ID	NSI THEO CONC CBENZ	NSI THEO CONC CTOLU	NSI RESULTS CBENZ(Dif)	NSI RESULTS CTOLU(Dif)	TAGA RESULTS CBENZ(Dif)	TAGA RESULTS CTOLU(Dif)
LC-0027	38.60	33.20	39.2(+1.6)	32.0(-3.6)	26.1(-32.1)	19.5(-41.3)
LC-0037	32.23	27.74	37.0(+14.8)	18.4(-33.6)	22.4(-30.5)	14.1(-49.2)
LC-0031	26.37	22.66	25.6(-3.0)	21.8(-4.0)	25.6(-3.0)	21.8(-4.0)
PEB-2	34.40	29.60	40.3(+17.2)	25.5(-13.9)	31.7(-7.8)	36.9(+24.7)
LC-0007	23.45	20.26	33.9(+44.3)	15.9(-21.3)	27.4(+16.8)	23.4(+16.1)
LC-0070	32.52	27.94	31.5(-3.1)	27.9(0)	32.2(-1.0)	28.7(+2.7)
LC-0040	47.80	40.77	43.5(-9.0)	33.9(-16.9)	48.9(+2.3)	34.8(-14.6)
LC-0009	47.60	36.64	47.4(-0.4)	23.8(-35.0)	43.8(-7.9)	39.1(+6.7)
LC-0012	31.44	27.02	36.7(+16.9)	26.5(-1.9)	33.3(+5.9)	29.6(+9.5)
LC-0003	28.78	24.75	36.0(+25.0)	24.6(-0.8)	39.6(+37.6)	35.2(+42.2)
LC-0063	42.13	36.52	40.4(-4.0)	25.4(-30.4)	40.6(-3.6)	36.6(+0.2)
LC-0047	28.27	24.50	34.0(+20.1)	23.1(-5.7)	21.6(-23.6)	13.4(-45.3)
LC-0039	28.81	24.96	26.2(-9.0)	25.5(+2.0)	31.6(+9.7)	30.9(+23.8)
PEB-1A	36.60	31.49	47.0(+28.4)	33.3(+5.4)	37.9(+3.6)	30.8(-2.1)
PEB-2A	37.55	32.28	41.2(+9.6)	30.6(-5.3)	36.3(-3.3)	31.7(-1.8)
PEB-1B	40.63	34.89	42.1(+3.6)	34.3(-1.7)	46.1(+13.5)	40.7(+16.6)
LC-0013	37.33	32.36	39.4(+5.50	26.8(-17.2)	42.5(+13.8)	31.0(-4.2)
LC-0025	34.67	29.78	35.7(+3.0)	28.9(-3.0)	34.3(-1.1)	29.5(-0.9)
LC-0026	41.07	35.27	32.3(-21.4)	32.3(-8.4)	42.7(+4.0)	38.8(+10.0)
LC-0052	33.60	29.12	38.2(+13.7)	31.3(+7.5)	42.0(+25.0)	36.2(+24.3)
LC-0069	37.33	32.06	39.1(+4.7)	33.4(+4.2)	41.0(+9.8)	36.6(+14.2)
LC-0072	31.47	27.03	34.2(+8.7)	26.8(-0.9)	32.5(+3.3)	29.4(+8.8)
LC-0066	37.33	32.66	34.5(-7.6)	30.1(-7.8)	41.0(+9.8)	36.9(+15.1)
LC-0013	37.33	32.36	39.4(+5.5)	26.8(-17.2)	37.4(+0.2)	27.5(-15.0)
LC-0030	37.33	32.36	34.4(-7.4)	29.0(-10.4)	37.9(+1.5)	34.1(+5.4)
LC-0033	37.88	32.88	39.2(+3.4)	27.3(-17.0)	36.9(-2.6)	32.2(-2.1)
LC-0049	30.40	26.35	32.0(+5.3)	23.1(-12.30	32.6(+7.2)	29.1(+10.4)
PEB-1B	40.63	34.89	42.1(+3.6)	34.3(-1.7)	40.2(-1.0)	36.2(+3.8)
PEB-2B	37.10	31.87	37.1(0)	30.2(-5.2)	40.0(+8.0)	37.8(+18.4)
LC-0040	37.30	32.36	41.7(+11.8)	28.7(-11.3)	42.9(+15.0)	37.9(+17.1)
LC-0003	28.24	24.27	34.5(+22.1)	23.4(-3.6)	30.0(+6.2)	27.1(+11.7)
LC-0056	35.17	30.23	41.5(+18.0)	29.7(-1.8)	39.9(+13.8)	35.9(+18.8)
LC-0012	33.57	28.86	36.1(+7.5)	29.6(+2.6)	37.5(+11.7)	34.0(+17.8)
LC-0020	43.71	37.88	40.6(-7.1)	33.8(-10.8)	35.0(-19.9)	30.9(-17.8)
LC-0039	38.70	33.26	36.5(-5.7)	33.3(+0.1)	30.2(-22.0)	27.7(-16.7)
PEB-1C	37.00	31.78	38.4(+3.8)	30.4(-4.3)	38.2(+3.4)	34.4(+8.2)

16L canisters are indicated by PEB in canister ID listings.

DISCUSSION

AVRAHAM TEITZ: What do you use for confirmation?

TOM PRITCHETT: We sample the air stream until we see the signal go back up for the ions we're looking for. And then, depending on the type of analysis we're doing, we'll pop either a Summa canister or use some other confirmation analysis. If we're doing time-weighted average sampling in conjunction, we use the time-weighted average results for confirmation.

But typically, the compound is an unknown. We can't really do too much, except a Summa canister off to the side, at the same time we're sampling. We go out with anywhere from two to four evacuated Summa canisters for doing these confirmation analyses.

AVRAHAM TEITZ: Would that be analyzed the standard way, by GC/MS?

TOM PRITCHETT: Yes. One of the things we're considering is having an on-board portable GC, so at least we have the confirmation by retention time.

UNIDENTIFIED PARTICIPANT: Does the sensitivity change by the same factor for different compounds?

TOM PRITCHETT: We haven't looked at all the compounds. The compound I described ionizes by charge exchange. The reason the sensitivity went down is that the source chemistries were in competition. As we increased the amount of water present, it actually scavenged the regent ions with greater ionization potentials.

I've monitored multiple parent ions for the same compound and seen the relative intensity of those parents, particularly oxygenated compounds, change through the day. In some cases, one parent, the M+ ion, will increase in sensitivity while another, the M-1, decreases. This work was with parent long only and was independent of any variation in fragmentation.

UNIDENTIFIED PARTICIPANT: Have you looked at using some internal standards, since you know what compounds you are looking for?

TOM PRITCHETT: When we know what we're looking for, we have considered using isotopic internal standards. There is so much unknown going on in source chemistry, we don't know how compounds track with each other. We haven't been able to do these comparisons under controlled conditions.

We are seriously considering using an isotope in surrogate standards to be continually doped into the mixture. If we see the intensities of those surrogates changing, we could do a series of spikes in that matrix in order to gather a data base on changes in relation to response, which is needed to start using actual internal standards.

UNIDENTIFIED PARTICIPANT: Do you have any experience with the atmospheric pressure source of the TAGA? Does it have similar problems?

TOM PRITCHETT: The group leader in our contractor staff came out of a consulting company that did an extensive amount of atmospheric pressure chemical ionization (APCI). They ran into some problems with ammonia and amines.. Also, Brian Stewart of the National Research Council has done some controlled humidity studies with an APCI source.

He started off with very dry air, and there was almost no sensitivity. As water was added, the sensitivity rose drastically and then started tailing back off. Initially there is no water chemistry, because there's no water present. The sensitivity tailed off once he started getting too much hydration. All you're doing is pushing the hydration up to higher levels. You actually decrease the acidity of your reagent ions, because as you hydrate a hydronium ion, its pH actually drops a little.

MR. PRITCHETT: What we're talking about is actually humidity effects before you do any declustering. It's the cluster itself that protonates the compound in the source, not the hydronium ion. For example, the 37 ion or the 55 ion is actually doing the protonation. As you increase the 57 in the source, versus the 37, you actually decrease the effective acidity of your reagent gas.

MARC WISE: Obviously, the way to get around these problems is to continuously inject an internal standard into the gas stream. Do you have a viable means of doing that at this time?

TOM PRITCHETT: As a matter of fact, we do. We're using gas standards to dope into our sample measures. We do hour calibrations in ambient air, so it's just a matter of putting a very low level, let's say to 10 ppb, of a continuous feed into the sample matrix. You want to make sure you pick some surrogate compounds that aren't going to cross interfere with some of your other compounds.

The main reason we haven't gone to internal standards is that we don't know enough about the charge exchange source chemistry to predict which compound tracks which. In other words, if I see this response go down for this compound, what does that mean for the response of compound Y?

Something else we found with these chemical ionization chemistries is that if you change the sample matrix, you drastically change your calibration.

I used to go out with this instrument, calibrate in ambient air, and then stick it in an incinerator, monitoring the stack gas. The CO_2 concentration and the absolute humidity concentrations are not comparable. We look for that now. If we change the reagent gas, or if the matrix changes, we do some type of QA/QC to verify that we haven't changed the response factors.

MARC WISE: So your response factors that you determined twice during the day and used as intermediates are in the presence of the compounds you're analyzing? You determine those with the compounds?

TOM PRITCHETT: Yes. We measure the response factors in the matrix before and at the end of the day. We do the spikes into the matrix – two-point spike. And it's always in the sample matrix that we're analyzing.

MIKE FINNIGAN: It seems that ionization is an exceedingly complex problem. You've mentioned there are three methods of chemical ionization – what compounds are ionized by what mechanism, what mechanism is affected by the presence of CO_2 or water vapor, and so on.

Why not add a short stage of chromatography in front of this to space out these compounds – to allow the chemistry in the source to be dominated either by chromatography, or some other technique, as you do in an ion trap, so that the chemistry in the source is a fixed one, and not just dependent upon the water that's coming in with the sample or the CO_2?

TOM PRITCHETT: That is an advantage of your system versus what we're dealing with. You've got your source chemistry stable. We haven't gone into depth in doing that, primarily because this problem was known for a long time. If I could figure out how to do it, (add a short GC and retain the calibration source chemistry) and make that transition quickly, I probably would shift that way, because I would like to be able to use some chromatography on the front end. It would really give me some real strong advantages being able to distinguish between compounds.

RESULTS FROM THE ENVIRONMENTAL RESPONSE TEAM'S PRELIMINARY EVALUATION OF A DIRECT AIR SAMPLING MASS SPECTROMETER

Robert E. Hague
Department of Environmental Science
Cook College, Rutgers University
New Brunswick, New Jersey 08903

Thomas H. Prichett
U.S. EPA Environmental Response Team
GSA Raritan Depot
Edison, New Jersey 08837

Kwong Cho
Roy F. Weston, Inc. (REAC)
GSA Raritan Depot
Edison, New Jersey 08837

Ben Shapiro, formerly of
Enviresponse, Inc. (EERU)
GSA Raritan Depot
Edison, New Jersey 08837

ABSTRACT

During the summer of 1987 an investigation of the Bruker MM-1 mobile mass spectrometer was performed under the auspices of the EPA Environmental Response Team (ERT) in order to evaluate this instrument's applicability for emergency response and Superfund-related tasks. The unit was tested with a series of ambient air samples spiked with mixtures of organic compounds over the low-ppb to low-ppm range. An evaluation of the instrument's suitability was made on the basis of sensitivity, specificity, ruggedness and overall usefulness under field conditions.

INTRODUCTION

The instrument evaluated in this paper is the Bruker mobile mass spectrometer model MM-1 manufactured by Bruker Instruments, Inc. The MM-1 is a quadropole mass analyzer and electron impact ion source mass spectrometer which has been designed specifically for use under field conditions. The instrument and its ancilliary data handling package is self-contained, and is designed to be ransportable and operable while mounted in a four wheel drive vehicle. During mobile operations, power is supplied using a rechargeable 24 volt DC battery.

Operation on a real-time analysis format. The air sample is drawn into the instrument at a constant flow rate in ambient air and analyzed instantaneously and continuously. There is no separation of organic compounds or sample preparation. All compounds are analyzed simultaneously. Analytical results, instrument parameters, and listings of identified compounds are displayed on a video screen and continuously updated. During routine air sampling, sets of four ion peak intensities representative of a given compounds are displayed as histograms on the screen on a real time basis. Histogram height varies as the base 10 logarithm of the ion's intensity. The intensity scale range allows measurement over 7 orders of magnitude. All results are normalized, so that direct comparison of measurements from all analyses can be made. Additions to the spectrum library may be made by either defining a compound in terms of ion intensity ratios entered from the keyboard, or by exposing the sampling head to the vapor of that compound, and selecting ion mass frequencies from the resulting spectrum. Printed copies of analyses, library contents and system status may be displayed at any time on the CRT or downloaded to a small panel-mounted printer.

Sampling is performed using a sampling line directly coupled to the mass spectrometer, both of which are operated by a simple control keyboard. (Figure 1) Samples are introduced into the system via heated sample head located at the end of the sample lilne. The sample head is a nickle gauze coated with a semipermeable silicone membrane. Samples are pulled through this membrane by a sampling pump at a rate of 1 to 3 cc/nimute. The membrane serves to protect the sample line itself, which consists of a 3.5 meter 0.32 mm quartz capillary column coated with an SE-54 Phase surrounded by an insulated, heated jacket. At the end of this line, the sample is drawn through a second silicone membrane and into the mass spectrometer. In the event of line contamination, there is a backflush system. The sampliing line is capable of temperature ramping and some primitive separation of compounds can be achieved. Once inside the mass spectrometer, the compounds are ionized utilizing electron bombardment by an electron source.

In general, gas chromatographic/mass spectrometer systems are designed to present individual molecular species to the mass spectrometer following their separation from the sample matrix on the chromatographic column. In real time analysis, such as is the case with the MM-1, the compounds are not separated and are presented to the detector simultaneously. The ions from different compounds are combined and the resulting ion mass ratio is the sum of the ions from all of the compounds present in the sample. This leads to the previously mentioned difficulties in compound identification and quantification. In most environmental analyses of compounds, the three most prevalent characteristic ion masses of each compound are utilized in identification. In an effort to circumvent the problems encountered in real-time analysis with identification, the MM-1 utilizes four characteristic ion masses and their abundance ratios. Even so, with complex mixtures of compounds, the detector has difficulties with identification, and false positive and false negatives are common.

EXPERIMENTAL

The MM-1 was tested over a range of concentrations representative of both chronic and acute emission levels of organic compounds in air. A dual sample dilution manifold was constructed to provide the capability of diluting cylinder gas standards in ambient air over the ppb to ppm range. The system consisted of two parallel sample dilution lines of differing diameters with side-tapped glass and Teflon sampling ports. Both manifolds use individually sized mass flow controllers at their discharge ends and share common diluant sources, (ambient air and zero air) common organic vapor sources and a common low pressure multistage blower. Use of ambient air as the diluant allowed evaluation of the instrument under actual daily variations in temperature, humidity, and background concentration. The manifold lines were sized so as to provide usable concentrations over a feasable sampling interval. Two lines were used. A 7/8 inch ID Teflon line for the high dilution line provided metered flow values of 30-150 liters/miln. for dilutions to between 5 to 100 ppb. A 3/8 inch ID stainless steel line providing metered flow rated of 2-7.5 liters/min. for vapor concentrations over the range from 1.0 to 10.0 ppm. Both lines were heat traced and maintained at 40 degrees C. Concentrations at each dilution were verified by gas chromatography before being presented to the MM-1.

The shared vapor sources were of two types: (1) Standardized NBS traceable multi-componant compressed gas mixtures that were metered through a mass flow controller into the sample lines for ambient air dilution to produce the desired concentration and, (2) a heated vaporization source for compounds which are unsuitable as pressurized cylinder standards. The vapor source was pairs of midget blass impingers containing the organic compound of interest kept in a thermostatted water bath. A controlled air fow was passed through the impinger train, saturated with vapor, and diluted to its final desired concentration with ambient air.

The evaluation of the MM-1 was divided up into four phases. Phase 1 evaluated the instrument's lilnearity and sensitivity by providing progressively higher dilutions of standard gas mixtures cylinder by cylinder over the test concentration range. A "detectability limit" for those compounds in that mixture determined. Phase 2 presented the instrument with unknown concentrations of known compounds within the list of compounds presented to in Phase 1. Phase 3 presented the MM-1 with mixtures of compounds from a list of non-cylinder-stable compounds, including aniline, pyridine and m-creasol. The analyst was not provided with information on compounds to be expected or their concentration. A list of the compounds present in each cylinder is given in Table 1.

RESULTS

Phase 1 testing indicated that sensitivity was chiefly limited by interferences from the other compounds present in the mixture. Typical high-sensitivity compounds were detectable at 10 ppb. (Table 2). The detectability of a given compound was a function both of the other compounds present and the ambient background concentration of organic materials. Complex mixtures create interferences which raise the detection limits considerably. Common-ion effects apparently prevented the MM-1 from recognizing some compounds even at the 10 ppm level. However, it should also be stated that the linearity of response for many of the compounds was quite good, with correlation coefficients exceeding 0.95 over three orders of magnitude. Typical response curves are shown in Figures 2 to 5.

Phase 2 the results of tests performed are given in Tables 3 & 4. In complex mixtures, both false positives and negatives were common. For those compounds whcih were correctly identified, quantitation error ranged from +2.2% to -39.1% and depended on the specific compound. Variation in response for replicate samples was less than 8%.

Phase 3 presented a series of mixtures to the instrument whose concentration and composition were unknown to the analyst. An effort was made to select compounds which are of interest at Superfund sites, but which were not available as cylinder gas standards. Calibration curves were not prepared for these compounds and the emphasis was strictly on qualitative identification . The results of Phase 3 are shown in Table 5.

OVERALL COMMENTS

•SENSITIVITY AND ACCURACY

When single compounds with no common ions are being analyzed, the sensitivity of the MM-1 under typical ambient conditions ranged from 10 to 25 ppb. The stability of the instrument is such that repeat readings over a period of time agree within a fraction of a response unit. Linearity of response was found to be good over the range of 10 ppb to 10 ppm for many compounds. As stated previously, mixtures of compounds sharing one or more common ions drastically reduces both the sensitivity and accuracy of the instrument. Accuracy was also found to be low where compounds not included in the target library were present in the mixture.

•PORTABILITY

Subsequent to the Phase 3 testing, the MM-1 was mounted in a four wheel drive vehicle and field tested. It was found that the durability of the unit was truly remarkable. After off the road use, the instrument still retained its calibration and full internal vacuum. The battery pack was found to generate sufficient power for a 6 to 8 hour operating schedule before recharging was necessary.

Setup time is minimal at about 15 minutes with an additional 30 minutes for calibration and sample line purging. The analysis time is approximately 15 seconds, with triplicate analyses in less than one minute.

•LEVEL OF OPERATOR TRAINING REQUIRED

The Bruker MM-1 is designed with extremely simple operating procedures based on a series of menus which are all accessable from a simple keyboard. This allows an operator to analyze ambient air samples with a minimum of training. It should be noted however, that although the instrument is simple to operate, the data have limitations and should be assessed by an experienced mass spectroscopost who is aware of potential interferences and the limitations inherent in real-time analysis.

The experienced operator may in some cases be able to recognize false positives and false negatives by reviewing the ion mass list and abundances of those ions. In complex mixtures of organic compounds, useful data may be limited. With this understanding, an operator will be better prepared to recognize any problems which may occur.

•RELIABILITY

The reliability of the instrument from a mechanical standpoint was exceptional. Over the course of three months, the only breakdowns were a leaking calibration gas valve and an electronics overload caused by a power failure and subsequent voltage surge. The manufacturer responded promptly in both cases, and had the instrument functioning perfectly within one day.

In order to evaluate the unit under true field conditions, during the last part of the study, the instrument was mounted in a four wheel drive vehicle and used as a mobile unit at a Superfund landfill site. It experienced no mechanical problems even while being operated under conditions of high temperature, high humidity and while being driven off-road. The data obtained however, again were limited in their usefulness by high concentration in the soil gas samples of a wide variety of miscellaneous hydrocarbons, which, given this instrument's lack of chromatographic capability allowed only a few compounds to be tentatively identified.

•OBSERVATIONS AND RECOMMENDATIONS

In the configuration used in this study, the instrument is not applicable to most site assessment work, unless it is known that a relatively small number of compounds known to be present, or if the compounds of interest are present at concentrations significantly higher than potential interferants. The instrument is designed for real-time air monitoring and performs well in this capacity. The complex mixtures of compounds which can be found in waste sites are likely to create identification problems with false negatives and positives occuring.

In the case of a chemical spill emergency, given knowledge of the compound or compounds released, the instrument would be the method of choice in delivering quick and precise data. Its transportability and ruggedness would allow a plume of vapor to be readily traced and quantitated. A new gas chromatographic attachment is now available. Although it was not evaluated in this study, manufacturer's information indicates that many of the problems found in this study should be resolved by this modification.

REFERENCES

(1) Bruker-Franzen, "Analytic GmbH," The MM-1 Mass Spectrometer User Manual. Bruker-Franzen Analytik GmbH, Bremen, West Germany, 1986, pp. 2-28.

(2) Bruker-Franzen, "Analytic GmbH," The MM-1 Mass Spectrometer User Manual. Bruker-Franzen Analytik GmbH, Bremen, West Germany, 1986, pp. 2-32.

TABLE 1.

CYLINDER GAS STANDARDS--PHASES 1,2

TANK A

Toluene
1,1,1-Trichloroethane
1,4-Dioxane
Acetone
1,2-Dichloroethane

TANK B

Vinyl Chloride
Benzene
Methylene Chloride
1,1-Dichloroethylene
Trichloroethylene

TANK C

Methyl Ethyl Ketone
n-Hexane
Methyl Isobutyl Ketone
Tetrachloroethylene
1,4-Dioxane

TANK D

Cyclopentane
Ethyl Acetate
1,1-Dichloroethane
1,1,2-Trichloroethane
Carbon Tetrachloride

TANK E

Chlorobenzene
o-Chlorotoluene

TANK F

Isopropanol
Ethyl Ether
3-Chloropropane
Styrene
Ethyl Benzene
Freon 11

Table 2. MM-1 Sensitivity and Selectivity of Compounds in Phase 1 Mixtures

Compound	Limit of Detection (ppbv)
Acetone	100
Vinyl Chloride	1000
Cyclopentane	10
Benzene	25
Methylene Chloride	10
Hexane	25
Ethyl Acetate	10
1,4-Dioxane	1000
Toluene	25
1,1-Dichloroethylene	25
1,1-Dichloroethane	100
Ethyl Benzene	5
Chlorobenzene	10
o-Chlorotoluene	10
Trichloroethylene	25
1,1,1-Trichloroethan	100
1,1,2-Trichloroethan	25
Tetrachloroethylene	25
Styrene	100
Trichlorofluoromethane	ND
Ethyl Ether	1000
Methyl Isobutyl Ketone	10000
1,2-Dichloroethane	100
Methyl Ethyl Ketone	ND
Isopropanol	ND
3-Chloropropene	ND
Carbon Tetrachloride	ND

ND--Not Detected Due to Common Ion Effects

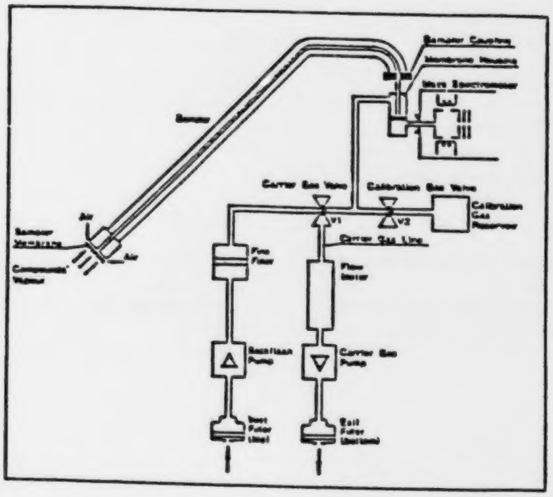


Figure 1. Schematic of the MM-1 Inlet System (1)

Table 3. Phase 2 Mixtures

Compounds	Conc. (ppb)	Identified	False Neg.	False Pos.
Acetone	500.5		x	
1,4-Dioxane	428.2		x	
1,2 Dichloroethane	476.7		x	
1,1,1 Trichloroethane	474.8		x	
Toluene	467.7	x		
Chlorobenzene	522.6	x		
o-Chlorotoluene	527.2	x		
Acetonitrile				x
Dichloromethane				x
Acetaldehyde				x

MM-1 Response: Unknown #2

Compounds	Conc. (ppb)	Identified	False Neg.	False Pos.
Benzene	133.7	x		
Vinyl Chloride	133.7		x	
Methylene Chloride	134.4	x		
1,1-Dichloroethylene	125.3		x	
Trichloroethylene	142.4		x	
Ethyl Benzene	264.7		x	
Ethyl Ether	249.3		x	
Freon-11	255.3		x	
Styrene	279.2	x		
Acetonitrile				x
Allyl Chloride	249.7		x	

MM-1 Response: Unknown #3

Compounds	Conc. (ppb)	Identified	False Neg.	False Pos.
Methyl Ethyl Ketone	124.0		x	
Hexane	158.5		x	
1,4-Dioxane	129.5		x	
1,1 Dichloroethane	247.0	x		
1,1,2 Trichloroethane	257.5	x		
Cyclopentane	245.1		x	
Ethyl Acetate	251.5	x		
Carbon Tetrachloride	253.0		x	
Tetrachloroethylene	143.2		x	
Acetonitrile				x
Methyl Isobutyl Ketone	131.1	◆		

◆ detected - not quantified

MM-1 Response: Unknown #4

Compounds	Conc. (ppb)	Identified	False Neg.	False Pos.
Vinyl Chloride	251.3	x		
Benzene	251.4		x	
Methylene Chloride	252.8		x	
1,1-Dichloroethylene	235.6		x	
Trichloroethylene	267.9	x		
Cyclopentane	564.1	x		
Ethyl Acetate	579.0		x	
1,1-Dichloroethane	568.5	x		
1,1,2-Trichloroethane	592.5	x		
Carbon Tetrachloride	582.2		x	

Table 4. Accuracy of Phase 2 Responses

Compound	Generated Concentration (ppb)	Measured Concentration (ppb)	Percent Deviation
Chlorobenzene	522	321	-38.5
Toluene	468	507	+ 7.6
o-Chlorotoluene	527	540	+ 2.5

Accuracy of MM-1 Response: Unknown #2

Compound	Generated Concentration (ppb)	Measured Concentration (ppb)	Percent Deviation
Benzene	134	137	+ 2.2
Dichloromethane	134	155	+15.5
Styrene	279	170	-39.1

Accuracy of MM-1 Response: Unknown #3

Compound	Generated Concentration (ppb)	Measured Concentration (ppb)	Percent Deviation
1,1,2 Trichloroethane	258	155	-39.9
Ethyl Acetate	252	219	-13.1
1,1 Dichloroethane	247	229	- 7.3
Methyl Isobutyl Ketone	131	NQ	-----

NQ = detected, not quantified

Accuracy of MM-1 Response: Unknown #4

Compound	Generated Concentration	Measured Concentration	Percent Deviation
Vinyl Chloride	251	170	-32.2
Cyclopentane	564	607	+ 7.6
1,1-Dichloroethane	569	555	- 2.5
Trichloroethene	268	165	-38.4
1,1,2-Trichloroethane	593	532	-10.3

Table 5. Phase 3 Unknowns

Unknown #1

	Concn. (ppm)	Identified	False Positive	False Negativ
Aniline	1.34			+
m-Cresol	0.5			+
Pyridine	45.0	+		
Ethoxyethanol	7.0	+		
Acetaldehyde			+	

Unknown #2

	Concn. (ppm)	Identified	False Positive	False Negativ
m-Cresol	0.5	+		
o-Xylene	79.0	+		
Aniline	6.7			+
Acetaldehyde	-		+	
Ethyl Benzene	-		+	

Unknown #3

	Concn. (ppm)	Identified	False Positive	False Negative
Chloroform	7.8	+		
Butyraldehyde	4.6			+
n-Hexane	6.0			+
n-Butanol	---		+	
Dichloromethane	--		+	

FIG. 2 METHYLENE CHLORIDE

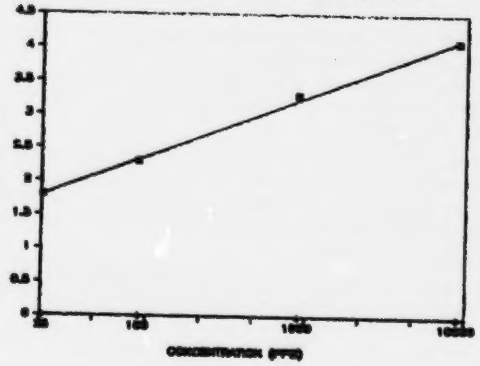


FIG. 3 O-CHLOROTOLUENE

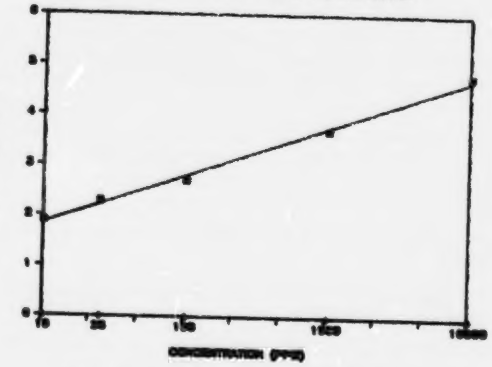


FIG. 4 1,1,2-TRICHLOROETHANE

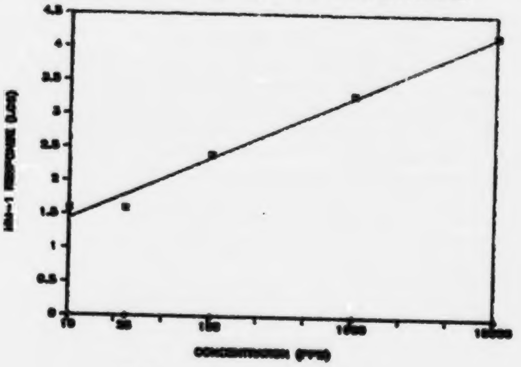
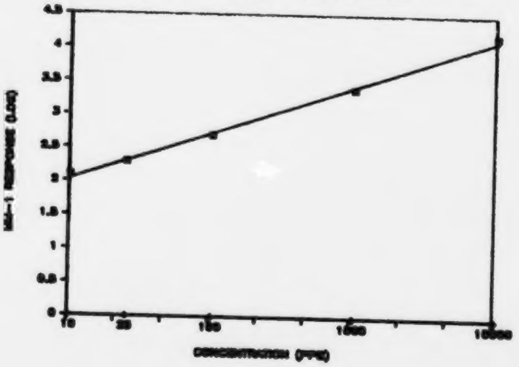


FIG. 5 CYCLOPENTANE



DISCUSSION

MIKE FINNIGAN: The samples that you picked and the volatiles and the artificial standards, consisted of four to six compounds. You got up to two of them, three of them, and so on. What is the real world when you go out to a site? How many compounds are you going to wind up seeing, and what's your prognosis about that?

TOM PRITCHETT: It depends. We typically run with four compounds per cylinder. We run two cylinders of mixtures. I have been tasked to go out and monitor for as many as 12 to 13 compounds simultaneously at a waste site. I have analyzed headspace samples (leachates) where I had the world come at me. You name it, it was there.

At other places, you're only looking for one or two compounds. And that's all you're really going to see. We gave it a worst-case scenario. I'd say a good 60% to 70% of the sites don't ever run into that mishmash. But because it worked well at one site, doesn't necessarily mean it's going to work well at another, particularly once you start throwing in the typical hydrocarbon soup you see around multiple-use landfills.

We said the compound mix shown was a worst-case scenario. Actually I've seen compound mixes that are much, much worse from a landfill. Three quarters of the compounds in that chromatogram were hydrocarbons (a hydrocarbon soup). You'll see the oxygenated hydrocarbons in there also, and some chlorinated compounds.

If PCE and TCE are in a landfill, and it starts biodegrading, you can start walking down the degrees of chlorination until you hit vinyl chloride and chloroethane. You'll see all levels of chlorination if you've got those two compounds, and you've got a biologically active landfill.

You'll also see all levels of oxygenation there – aldehydes, ketones. That is a real landfill.

You can have a very clean site at a spill, or it could be a multi-use landfill where you have the world thrown at you.

ARTHUR BOYER: I've wondered if you've developed any methods or rules of thumb when to use what instrument? For example, should I use GC/MS? Should I use MS or should I use MS/MS?

TOM PRITCHETT: I don't think anyone who does this work has really locked on what to do when. As you learn from experience, you find certain things work at different sites. New technologies come out. I do things now for soil gas analyses that I wouldn't even have tried two or three years or six months ago. I'm always finding new tools to use and I'm learning more about the tools that I've got. I'm also realizing maybe this one tool wasn't as good as I thought it was. I can look back at what I did a year ago, or two years ago, I realize now what was occurring then that I just didn't see then.

JOE SOROKA: When you do some GC/MS, you try to match the peaks you get off the GC with the library TIC and use your own intuition and knowledge to look at the spectra to define what that particular component might be.

Are there other techniques with these kinds of direct-sampling air spectrometers that don't have the separation advantages that you get with a GC at the forefront? Or can you feel confident that you've possibly got most of the stuff? What would happen if you have a sample which may have things such as tetraethylene lead compounds, which probably are not in your library, and were totally unexpected? We have found them in certain samplings.

TOM PRITCHETT: If I just had one spectrum to look at, there are certain ions that are fairly universal and there are others that you just can't make any sense of. Some compound classes will stick out, and you can pull them out fairly easy from a real mishmash. Others you may very well end up missing compounds because you can account for all the ions for the compounds that you are seeing. But there may be something else hidden, because unless you do really quantitative spectral subtracting, the compounds may be lost in the differences of what you're looking at. It depends on how complicated the spectra are. That's why if you're doing unknown work, you should use GC on the front end. By the way, this is a problem that occurs with any direct-air sampling instrument.

JOE SOROKA: On the Bruker, for example, is there an algorithm within their software that can identify or account for all of the peaks that are in the spectra, except for particular ones, and highlight them so that you can take a look at them, and try and figure out where they come from?

FRANK LAUKIEN: When you come to a site, and you're not sure what you're looking for, we recommend starting in the single-ion monitoring mode. In many cases, the compounds you're monitoring for will be identified and quantitated without any additional interference.

Then there are cases where you see there are some identifications, and there's a lot of unidentified ion activity on the screen. The next step is to switch from single-ion monitoring to full-scan mode to see whether there are some compounds which you weren't monitoring for in single-ion monitoring mode. That may result another range of problems.

However, you will run into those problems where there is a lot of interference – even in the full spectral mode, there is too much interference for identification. Or as you've described, there might be some additional ions which simply don't fit into any picture. In this case, you switch over to the chromatography.

Introduction to the Session on Immunochemical Methods

Jeanette Van Emon, Chairman

I would like to begin the session by explaining the Agency's efforts in immunochemistry. EMSL-Las Vegas is the lead laboratory within the Agency for immunochemical methods, and our program consists of two facets – development of immunoassays and the evaluation of these techniques.

Our in-house efforts are partially conducted through Lockheed, ESCO, and we've just had the opportunity to hire Richard White, who comes to us from industry with the knowledge of development and evaluations of immunoassay kits. We are also have efforts through the University of Nevada – Las Vegas, Environmental Research Center by Kaz Lindley an analytical chemist who is eagerly embracing immunoassay techniques as well as helping us out with conventional wet chemistry. Development efforts are also supported by our contractor, Acurex, who is busy preparing work for us now. We have students from UNLV, particularly Julie Alamo, who assists me in just about every detail of my program.

Our in-house efforts are supported by the U.S. Department of Agriculture (USDA). We have an inter-agency agreement with them through the Food, Safety and Inspection Services. We are also networking among other governmental agencies.

We have cooperative agreements with the University of California at Davis with Drs. Bruce Hammock and Mark Kurth. Those of you familiar with immunoassay for environmental contaminants are already quite familiar with the name of Bruce Hammock. We're very fortunate to have these laboratories intimately involved in our program. Right now they are developing methods for analyzing nitro aromatic compounds.

We also have a cooperative agreement with the University of California at Berkley, the hybridomas facility headed by Dr. Alex Karu. This is a very fine monoclonal laboratory. We're also fortunate to work with this facility.

We had a cooperative agreement just recently awarded to Westinghouse Bio-Analytic Systems for developing immunoassays for some of the aromatic hydrocarbons.

We are also working with the private sector in coordinating evaluation studies – again, with Westinghouse Bio-Analytic Systems. We just finished an evaluation study for their immunoassay on pentachlorophenol, and now we are ready to go to our next step, the field demonstration.

We are working on evaluations with other governmental agencies – the USDA evaluations criteria committee and with the Association of Official Analytical Chemists (AOAC). We have proposed Agency guidelines on evaluation studies. A general referee for immunochemical methods has recommended that these guidelines be incorporated further into AOAC's methods committee's guidelines on evaluation of immunoassays. And we are beginning to work with the FDA, which probably stems from the efforts of the Office of Technology Assessment and their recent assessment on immunoassay.

Regarding the developmental side of our program, there are many reasons the Agency needs to develop or wants to develop immunoassay techniques.

First, the technique is easily amenable to analyzing human body fluids and biomarkers, so exposure assessment studies become very real. Immunoassays have a high sample capacity so you can get data in real time. And you can study animal populations around Superfund sites, or even human populations.

The technique is rapid. You can perform analyses on site, or you can outfit a mobile van and use laboratory-type based immunoassays. For Superfund sites, remedial actions and designated hot spots, can be monitored.

Immunoassay is capable of analyzing some products of biotechnology. In fact, for analyzing products of genetically engineered microorganisms, immunoassay may really be the only method of choice.

Our evaluation process works like this. For immunoassays submitted to the EMSL-Las Vegas, there are certain developmental criteria we would like to see fulfilled before we undertake an in-depth evaluation study.

One of these is that the assay is well characterized, or mature, has a standard operating procedure, accompanying QA/AC, data quality objectives, and so on. Depending upon the fulfillment of these developmental criteria, the next step would follow.

This would be either a laboratory confirmation, or a laboratory evaluation. If the assay is not well characterized, then the Agency would do a very minor type of evaluation study, or a preliminary evaluation.

Assays that are well characterized undergo a more detailed evaluation. After fulfilling a successful single-laboratory or multi-laboratory evaluation, the assay would go out on site. We have several demonstrations planned for the upcoming year – first, the pentachlorophenol, which could develop into a rather large study for providing some useful data on pentachlorophenol degradation, as well.

The important part of immunoassays, or any new technology, is implementation. So how do we do this? The Agency is working on this, as well.

First is the validation or evaluation of immunoassays, for which the Agency has an ongoing program.

Next is to introduce immunoassays into analytical laboratories. We also have efforts in this area. We recently participated in an FDA-sponsored workshop on immunoassay technology. We assisted the Congressional Office of Technology Assessment (OTA) in their assessment of immunoassays which they term, an emerging technology. I was fortunate to present a seminar to the OTA in Washington, D.C. a couple of months ago.

The Agency's immunoassay program was chosen as a subject for a computer-animated graphics program package. We are hoping that this can be used as a first-level training tool for persons who are interested in immunoassay, to be followed up with more detailed training programs.

The selection of initial compounds is important, as we want to make sure that we're giving the technology a fair assessment. The problems with new technologies are that you give them compounds that are impossible to analyze by other means. Immunoassay is amenable to a wide range of compounds, probably more so than any other analytical technique. However, it is important to choose the compounds for assay development that will also fulfill Agency and environmental monitoring needs.

We have run announcements in *Commerce Business Daily* aimed more at the business community, and in *Science*, aimed at academicians, to find out what has already been developed and who is working on this type of technology, so we can make more effective use of our resources. In fact, these announcements resulted in several unsolicitated proposals.

We're compiling a list of assay systems that have already been developed, and also a list of compounds of high priority for immunoassay development for the Agency.

DELIVERY SYSTEM FOR RAPID, SEMI-QUANTITATIVE ANALYSIS OF LOW MOLECULAR WEIGHT CONTAMINANTS AND RESIDUES

Philip L. McMahon
Director, Research and Development
IDEXX Corporation
Portland, Maine 04101

Robert Suva
Research Scientist
IDEXX Corporation
Portland, Maine 04101

Chris Brooks
Project Engineer
IDEXX Corporation
Portland, Maine 04101

ABSTRACT

Current testing protocols and assay systems for rapid screening of samples for the presence of a contaminant or residue often require auxillary equipment and/or reagents. This precludes their use in routine, field surveillance programs. In addition, functional characteristics often require critical timing and volume measuring steps.

Here we report on a self contained test system which offers features of self-measuring of reagents, in addition to internal controls for validating performance of the assay. The device itself can be modified to allow semi-quantitative as well as yes/no results. Descriptions and performance characteristics of the test system will be discussed.

INTRODUCTION

The intent of field testing is to rapidly screen samples for the presence of a compound of interest. When presumptively identified, the sample can be sent to a laboratory for confirmation and further identification. From this premise, field tests should be specific to correctly identify the compound, sensitive to the appropriate level and easy to perform to allow screening of a large number of samples.

In field testing situations, instrument and assay reliability are of paramount importance. In addition to these concerns, any additional technique sensitive procedures will yield inconsistent results. Environmental contaminants lend themselves to analysis by immunoassays. However, immunoassays, while often being easy to perform in field situations, have required auxillary equipment such as measuring pipets, washing equipment and instruments for readout.

Recently, delivery systems for immunoassays have appeared which offer some advantages in ease of use. However, they still suffer limitations of additional equipment and reagent requirements. The optimum system would be a zero technique immunoassay which integrates reagents and the delivery system and which is self-contained and disposable.

DELIVERY SYSTEM DESCRIPTION

The system consists of three general components. The device is a disposable, self-contained unit capable of measuring sample and retaining any excess reagents within the body. The tray contains appropriate wells for all reagents necessary to perform the test. The final component is the reagent set, premeasured and sealed in the tray.

The device consists of two, initially separated, absorbent materials. These are contained in a plastic body with a test head for sample/reagent entry and a depressable plunger for activating the system. The first absorbent takes up a premeasured volume, independent of starting sample volume. The sample is absorbed through ports in the test head which pulls all the volume through the bioreactive zones. The head therefore can vary in design depending on the application. If two ports are available, one can be for assay validation and calibration, the second serves to detect the analyte. In this configuration, if color develops in the calibration port, the reagents are functional and steps have been followed correctly. Color develops in the sample port proportional to the analyte concentration. By adjusting the calibration level to equal the cutoff of the test, then the presence or absence of analyte at that level is made by direct visual comparison of the color in the sample port to the calibration port.

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Because the calibration port is subjected to the same environmental conditions as the sample, including the sample matrix, conditions will be equivalent in each test zone, removing any temperature or matrix effects.

Multiple ports in the test head are another possible configuration. The ports can serve to simultaneously measure separate analytes or serve as multiple calibration levels. Thus, calibration can be set at an upper and lower limit of concentration of the analyte being measured.

A prefilter can be attached to the test head which will remove any particulate foreign matter from the solution prior to entry into the device. The tray can be designed to remove the prefilter after the sample incubation step.

The second absorbent serves as a reservoir for waste. Any sample or reagent that is pulled through the ports will be retained, removing the need for auxillary washing equipment or waste receptical.

The tray itself consists of separate wells into which premeasured volumes of reagents have been dispensed. The assay procedure calls for removing the sealing film, adding the sample, and sequentially moving across the tray, subjecting the test head to the various reagents. By this means, the test head can be exposed to sample, conjugate, wash solution, substrate solution (if an immunoassay) and stop solution (if required to stabilize the endpoint of the reaction).

The reagents themselves consist of antibodies or binding proteins of characterized activity, conjugate to detect the analyte, appropriate wash solution to remove any unbound materials, substrate solution to visualize the bound enzyme, and, if appropriate, sample diluent. The sample diluent can be used to dilute any interfering substances. This increases the utility of the assay system by allowing sample extraction to occur under relatively harsh conditions to insure dissolution of the analyte. These chemicals can then be diluted to a point where they no longer interfere with the biological activity of the assay.

REDUCTION TO PRACTICE

The utility of the test system has been assessed by applying the technology to a variety of systems, each with separate constraints on sample type and sensitivity requirements.

One assay developed required part per billion level sensitivity and organic solvent extraction to solubilize the analyte. The analyte was Aflatoxin B1, a product of fungal contamination in feed comodities. The extraction procedure developed consisted of grinding the sample in methanol:water (70:30). The reagents included antibody to Aflatoxin B1 which was raised in rabbits and passively adsorbed onto the solid support. The conjugate was Aflatoxin B1 conjugated to alkaline phosphatase, indoxyl phosphate was used as the substrate. Calibration intensity was adjusted to represent a signal level equivalent to 20 ppb Aflatoxin B1 in the sample. The final test protocol was as follows.

1) Sample (25 g) is ground in 100ml methanol:water (70:30) for 5 minutes.
2) Sample extract was then placed in the first well in the tray and the device was inserted.
3) Sample and device were allowed to incubate for 3 minutes.
4) The device was removed from the sample well, the secondary absorbent was then pressed into contact with the primary absorbant and the device was placed in the conjugate well (prefilled with 300 ul of conjugate) and subsequently incubated for 1 minute.
5) The device was removed from the conjugate well and placed in a wash well containing approximately 500 ul of wash solution. Following absorption of wash reagent the device was removed.
6) The device was placed in a substrate well for 15 seconds, removed and allowed to develop for 1 minute.
7) The reaction was stopped with water or stop solution.
8) The color intensity of the calibrator port was compared to that of the sample port.

The assay as described is a competitive immunoassay. The presence of analyte in the sample will therefore compete with the conjugate and decrease the color intensity of the sample spot. The calibration spot develops color independent of analyte concentration and sets a reference level of color. If the sample has less than 20 ppb Aflatoxin B1, the color intensity of the sample spot will be greater than the calibration spot. If the sample spot color intensity is less than or equal to the calibration spot, the sample is presumptively positive for the toxin.

The assay works well in the presence of high organic solvent (70% of methanol) and has shown no sample matrix effects from corn, peanuts or peanut butter. Current procedures for Aflatoxin B1 include thin layer chromatography or high pressure liquid chromatography. This test system for Aflatoxin B1 correlates well with these procedures.

Another application of the technology was developed to detect the antibiotic penicillin in milk samples. In this case, a prefilter was used to remove fats from the milk. The test consisted of incubating the milk sample in the presence of the biological, then allowing the mixture to enter into the device. The entire protocol is as follows:

1) Add 7 drops (0.25 ml) of milk with disposal plastic pipet to the first well contianing the conjugate and allow to incubate for 5 minutes.
2) Remove device leaving the prefilter in the first well and insert device into the second well and incubate for 3 minutes.
3) Insert device into wash well until all liquid is absorbed.
4) Insert device into substrate for 15 seconds, remove and allow to develop color for 3 minutes.
5) Stop reaction and read results.

The principles of the test are to allow any analyte present in the sample to bind to the conjugate and therefore prevent the subsequent binding of conjugate to penicillin covalently coupled to the test device, washing excess reagents through the test head and developing color. If penicillin is present in the sample being tested, then the sample port color intensity will decrease in proportion to the analyte concentration. By visual comparison of the color intensity of the calibration port to the color in the sample port, the sample can be classified as negative or presumptively positive for penicillin. The calibration level was set at the action level of penicillin (5ppb).

Existing methodologies for detection of penicillin include culturing with the organism Bacillus stearothermophilus or a binding assay using radioactively labelled penicillin. The correlation between all methodologies was excellent.

CONCLUSION

The availability of immunological reagents specific for contaminants and residues coupled with a convenient delivery system allows assays to be developed which can accurately detect analytes in a variety of sample types. Prefiltration by the device itself and subsequent containment of the solutions provides ease of use features which should make environmental monitoring more practical. Organic solvents to some extent can be tolerated by the biologicals; if not, then dilution of the sample to reduce the solvent concentration can be accomplished. The net result should be tests which allow expanded surveillance for contaminants by individuals not as skilled as trained laboratory personnel.

DISCUSSION

PETER DUQUETTE: How do you distinguish between the closed-ring penicillin and the open-ring penicillin?

ROBERT SUVA: The open-ring penicillins don't bind to the binding protein that we're using.

"Fieldable Enzyme Immunoassay Kits for Pesticides"

Peter H. Duquette
Patrick E. Guire
Melvin J. Swanson
Bio-Metric Systems, Inc.
R & D Division
9924 West Seventy-Fourth Street
Eden Prairie, Minnesota 55344

Abstract

Receptor proteins (especially antibodies and enzymes) have been demonstrated useful for rapid, convenient detection and semiquantitative analysis of pesticides. BSI has developed a rapid, disposable, self-contained, sensitive EIA device designed to allow untrained personnel to test for pesticides or other specific environmental contaminants in water or soil. The analyte in the test sample competes with an enzyme-analyte conjugate for a limited number of immobilized antibody sites. This Pinch Test format can detect paraoxon at one micromolar in water, with positive results indicated by clearly visible color development within ten minutes. It is operational in salt, brackish, and fresh raw water. This format is designed to have all dry components and to have an ambient shelf life of greater than one year. The format is readily adaptable for use with other environmental contaminants.

Introduction

Until recently, the analyses of pesticides has been based mainly on conventional chromatographic (i.e., GC, HPLC) and colorimetric techniques. The development of immunochemical procedures such as radioimmunoassay (RIA) have made it possible to analyze low concentrations of pesticides by combining immunospecificity with the sensitivity of radiochemistry (1-7). However, because of the inherent disadvantages involved with using radioactive materials (i.e., disposal of radioactive waste, possible health hazard, and use of expensive counters), there has been an interest in developing related nonisotopic immunoassays. An excellent alternative is the use of an enzyme as a nonisotopic label and recently solid-phase enzyme-linked immunosorbent assays (ELISA's) have been described for pesticide residue analyses (8-12). These assays circumvent the hazard and waste disposal problem associated with the use of radioisotopes, yet are comparable in sensitivity to RIA. An additional advantage to the use of antibodies versus conventional chromatographic techniques is that of high specificity of the antibody for the analyte, thus often avoiding extensive initial extraction of the lipophilic pesticides from the sample (13). The enzyme immunoassay procedures have many advantages of the RIA (i.e., specificity, sensitivity), but require only inexpensive equipment. Possibly the greatest advantage of enzyme immunoassays is that they can be adapted to either automated or fieldable methods (14).

Experimental Approach

Bio-Metric Systems, Inc. (BSI) has developed and is in the process of demonstrating a rapid enzyme immunoassay (i.e., Pinch Test) for the detection of organophosphate pesticides. The Pinch Test could also be easily adapted to the measurement of other environmental pollutants. The tasks required to develop the test for detecting organophosphate pesticides include: 1) preparing suitable derivatives of organophosphates that can be coupled to proteins in such a way that specific antibody can bind to them with high affinity; 2) preparing conjugates of the organophosphate derivatives with an appropriate enzyme derivative. The resulting conjugate must have suitable properties that allow rapid binding to immobilized antibody (a function of the number of haptens coupled and specific methods of coupling) and good recovery and stability of enzyme activity; 3) immobilizing antibody in a suitable form to a solid support such as cellulose; and 4) optimizing the components of the test (e.g., signal-generating enzyme).

Previous work at BSI has indicated that a more stable analog of paraoxon (i.e., diethyl 4-aminobenzylphosphorate) (DABP) (Figure 1, 3) exhibits excellent cross-reactivity with paraoxon antisera. Analogs of DABP were synthesized for use in preparing a suitable enzyme-hapten conjugate. The DABP was reacted with succinic anhydride to attach a carboxyl group and a spacer to the 4-aminophenyl group (Figure 1, 4). This compound (Figure 1, 4) was then reacted with N-hydroxysuccinimide (NHS) and dicyclohexylcarbodiimide (DCC) to form the activated N-oxysuccinimide ester (NOS) which can be easily coupled to various biomolecules.

Antibody specific for paraoxon was purified from antiserum that had been prepared by immunizing rabbits with a bovine serum albumin-paraoxon

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conjugate. The immunogen had been prepared by coupling diethyl-p-aminophenylphosphate (Figure 1, 2) to BSA by diazotization as previously described (9). The antiserum was fractionated by precipitation with 40% saturated ammonium sulfate and further purified by affinity chromatography on Sepharose-DABP. The crude IgG preparation was passed through a column of DABP-Sepharose in 0.01M 2-(N-morpholino)ethanesulfonic acid (MES) buffer at pH 5.0. After washing through the unbound protein, the specific antibody was eluted with 0.1M acetic acid and collected in tubes containing 0.1 ml of 1.0M $NaHCO_3$ at pH 9.0 to neutralize the antibody solution. The antibody was evaluated using the following ELISA method. DABP coupled to human serum albumin was adsorbed onto polystyrene microtiter plates. The antibody preparation was added and plates were incubated for one hour. After incubating, peroxidase-labeled anti-rabbit IgG was added and plates were incubated for one hour a second time. The plates were then washed with 0.05% Nonidet P-40 in PBS followed by addition of H_2O_2 and 2,2'-azino-bis(3-ethylbenzthiazolinesulfonic acid (ABTS). After twenty minutes the plates were read at 405nm with a microtiter plate reader.

Because of the instability of the paraoxon, the more stable DABP derivatives were used to prepare enzyme-hapten conjugates. These conjugates were determined to have excellent immunological and enzymatic activity. Recently, we have prepared spacer-modified glucose oxidase conjugates with various haptens which has resulted in greater stability and faster binding of the enzyme-hapten to the immobilized antibody compared to conjugates of native GO. The DABP or carboxylic acid derivative (4) can then be coupled to GO or modified GO by any one of the following methods: a) direct attachment of the DABP analog (4) (free carboxylic acid moiety of the succinic acid spacer) to the amines of the protein by use of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), a water soluble activated ester (i.e., sulfo-NOS), or coupling of the N-hydroxysuccinimide ester (i.e., NOS) of this hapten by established methods; and b) by direct attachment of the DABP by diazotization to the enzyme or modified enzyme.

Assay Development

Following antibody evaluation and synthesis of the enzyme-labeled hapten, the components are being tested and analyzed using an "enzyme-receptor Pinch Test." The "Pinch Test" was developed at BSI and is currently being developed into assay kits for drugs and naturally occurring low molecular weight toxins (Figure 2). The Pinch Test is a non-instrumented apparatus for qualitative or semi-quantitative determination of an analyte from biological fluids or environmental samples. In general terms, the format consists of two or more reaction zones which contain the appropriate reagents in liquid permeable solid media. These reaction zones are placed in such physical arrangement as to allow control over the sequence and time of exposure with test samples. The EIA has been miniaturized to maximize speed, portability, and ease of use. It is capable of detecting concentrations as low as 1-10 ng/ml of one or more analytes from biological or environmental samples on a single strip simultaneously.

The test format (Figure 2) consists of four parts: 1) antibody disks (A); 2) read-out disks (B); 3) absorbent blotting reservoir (C); and 4) a tube containing lyophilized enzyme-hapten conjugate (D). The antibody disks (A) contain immobilized antigen-specific antibody, while the read-out disks (B) contain: an immobilized enzyme; the dye; and a substrate for the enzyme-hapten conjugate. A reservoir (C), containing an absorbent pad is located beneath the antibody disks. An enzyme-hapten conjugate of the analyte is lyophilized and contained in a small tube (D). The user simply reconstitutes the lyophilized conjugate (D) to a specified volume with water, allowing the conjugate enough time for complete dissolution (ten seconds). Next, five drops of sample are applied to the antibody disks and incubated. The disks are washed with five drops of PBS or water to remove any extraneous material. One drop of the reconstituted conjugate is next added to the antibody disks (A) and incubated for one minute. The user then folds the top plate (Segment 1) containing the read-out disks (B) over the bottom plate (Segment 2) containing antibody disks (A), and pinches for approximately three seconds. The results are read in five minutes with a positive result being indicated by color formation. This assay format has distinct advantages over many other assays. For example, the sample size is not limiting because the antibody disk can be exposed to a relatively large volume of sample (up to 1 ml). This allows the antibody to bind any analyte residue which may be in the sample, thus increasing the sensitivity of the assay. Secondly, the wash step with PBS allows any possible interfering substances still present in the sample to be washed out of the antibody disk, thus reducing the possibility of non-specific color development. Additionally, the enzyme-hapten conjugate can be added after the sample, thereby increasing sensitivity. Finally, this format allows one to use built-in controls and can be adapted as a multi-toxin assay.

Since antibody and enzyme activities are affected by environmental factors (e.g., temperature, humidity), it is difficult to prepare a rapid enzyme immunoassay suitable for field use. However, we have demonstrated that antibody and enzyme activities can be maintained at 80% efficiency after storage at 70°C for 14 days. One method to achieve kit fieldability is to incorporate an internal reference which responds to environmental factors but is independent of the presence of analyte. Such a reference can be incorporated into our assay format by the inclusion of a control anti-enzyme binding region with the immobilized antibodies against the label enzyme.

Summary and Conclusions

Data from the above developmental experiments indicates BSI can produce a sensitive and convenient screening test for organophosphate insecticides. BSI has already developed similar EIA's for various drugs of abuse (i.e., cocaine, morphine, phenobarbital) with sensitivities of 1-10 ng/ml. It is believed that the assay format could easily be adapted to measure low levels of environmental chemical hazards such as polychlorinated biphenyls, pentachlorophenol, and other compounds found on the EPA Priority Chemical List.

Acknowledgements

The authors wish to acknowledge the following support: USEPA SBIR Contract No. 68D80035.

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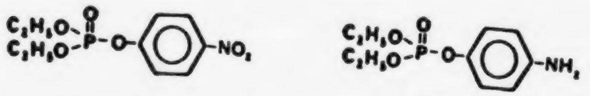
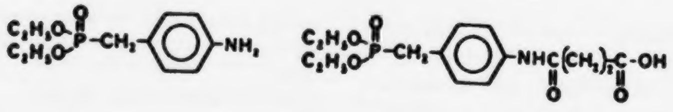
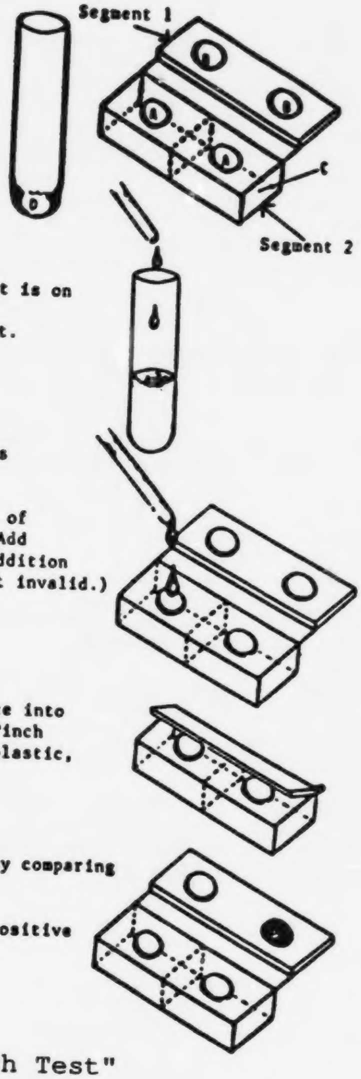


Paraoxon (1) Aminoparaoxon (2)



DABP (3) DABP-Succinic acid (4)

Figure 1. Paraoxon Analogs



Parts:
A. Antibody Disk
B. Read-out Disk
C. Blotting Reservoir
D. Lyophilized Conjugate

Procedure:

1. Resuspend Conjugate:
   - Open conjugate tube making sure pellet is on the bottom of tube.
   - Add 12 drops PBS with disposable pipet.
   - Replace cap and mix thoroughly.

2. Sample, Wash, Conjugate Application:
   - Take a disposable pipet and add 5 drops sample to test well.
   - Add 5 drops PBS to wash the test well.
   - Take disposable pipet and add one drop of resuspended conjugate to test well. (Add conjugate carefully and slowly. The addition of two or more drops will make the test invalid.)
   - Wait one minute.

3. Pinch:
   - Pinch the test by folding read-out piece into the test well while holding upright. Pinch all the way until plastic is touching plastic, hold for 2-3 seconds, and release.

4. Read Result:
   - Read result 5 minutes after the pinch by comparing to color chart.

     0,1 = negative   2 or darker = positive

Figure 2. The "Pinch Test"

DISCUSSION

HANK WALSH: How much time and effort is involved with coming up with a new assay? Suppose I wanted to detect PCB's instead of organophosphates?

PETER DUQUETTE: It takes a while. You have to make the antigen and conjugate. Then you have to get your titers up. The conjugate must have good immunological activity. That's been a problem. We have some "spacer technology" where we couple the analyte to the active enzyme and splice them. That allows us to have good immunological activity. The time that it takes to develop these is quite significant. How long it's going to take to do the whole assay will vary. The read-out disk is the same in all the assays, so those basically are stable. You still are going to have to go through and check out your conjugate and your antibody.

HANK WALSH: What would it be – half a man-year to five man-years?

PETER DUQUETTE: We have a development contract with a private company now, and we proposed for five different analytes that would take a one-person-level effort for six months.

RICHARD WHITE: Regarding the data on the stability of the enzyme, was that an enzyme that was in association with the solid phase or entrapped in the solid phase?

PETER DUQUETTE: That enzyme is immobilized, and there are some stabilizers added. It's a combination of polymers and proteins, and that's about all I can tell you.

RICHARD WHITE: In the pinch test that you talked about, the conjugate would be not really immobilized in the solid phase, right?

PETER DUQUETTE: No.

INTEGRATED IMMUNOCHEMICAL SYSTEMS FOR ENVIRONMENTAL MONITORING

J. M. Bolts, S. E. Diamond, J. F. Kolc, S. H. Lin and F. J. Regina
Allied-Signal Corporate Technology, P. O. Box 1021R, Morristown, NJ 07960
and
P. G. Koga, G. C. Misener and J. C. Schmidt
Bendix Environmental Systems Division, P. O. Box 9840, Baltimore, MD 21284

ABSTRACT

The physiological functions of antibody molecules include the specific recognition of foreign materials, and the potentiation of the host's immunological defenses. The extraordinary specificity of the natural immune response can be exploited and adapted for environmental monitoring by designing integrated analytical systems which combine immunochemical elements with advanced sensor instrumentation.

In this paper, our prototype immunodetection systems, suitable for environmental field use, are described. Two different integrated immunochemical systems are discussed, one based upon a chromatographic approach and the other utilizing an optical fiber immunosensor design.

Using these technologies, a wide range of analytes have been successfully assayed in both air and water sample streams, including a variety of toxic chemicals and hazardous microorganisms. The specific example of bacterial detection is used to illustrate the broad applications of these technologies, and the options available in the design of customized immunoreactor/sensor component systems.

Key Words: Immunochemical sensor, optical fiber, size-exclusion chromatography.

INTRODUCTION

Integrated immunochemical sensing systems represent a most attractive route to the development of versatile and sensitive instrumentation for environmental monitoring applications. In our laboratories, two prototype immunodetection systems, suitable for environmental field use, are under development. One design features separate immunochemical and detection modules. In this system, air or liquid samples are first analyzed in an antibody reactor, and then the products of the immunoreaction are conveyed to a sensor module for quantitation and display. In the alternate design, the immunoreaction occurs directly on the surface of a transducer device.

This paper will describe a chromatographic sensor system based on the first design, and a fiber optic system exemplifying the second design. The performance capabilities of both immunodetection systems will be illustrated with reference to the immunochemical detection of low levels of bacteria in environmental samples.

SYSTEM DESCRIPTION

Our integrated immunodetection systems are modular in design, and can accomomdate a variety of interchangeable sensor modules. A common "chasis" module is comprised of a sample acquisition system, air and liquid transport systems, and a host electronics and signal processing apparatus. Battery packs for power in the field, and reservoirs of buffers and immunoreagents, are also aboard the chasis module. In contrast, the individual sensor modules contain only components which are unique to their respective operating requirements. This modular system design allows the user maximum flexibility to select the sensor option best suited to his particular needs. In addition, the modular design helps to ensure that future advances in sensor technology can be readily adapted for use with immunodetection units already in the field.

The overall system is designed to be portable, approximately one cubic foot in volume, and capable of unattended field operation over a twenty-four hour period. In addition, the system is designed to respond within minutes to specified threshold levels of targeted molecules and organisms.

CHROMATOGRAPHIC SENSOR MODULE

A technique designated Size Exclusion Chromatography (SEC) has been developed in our laboratories for application to the rapid immunochemical detection of microorganisms and other large analytes. The basic principle of the SEC method is depicted schematically in Figure 1. Note that the SEC technique distinguishes between large and small analytes, and that large analytes elute rapidly from the column while smaller analytes are delayed within the column and elute later. When used in conjunction with an immunochemical pre-incubation, an SEC column can rapidly separate the larger antibody-antigen complexes from the smaller, unconjugated antibody molecules, as long as there is a sufficient size difference between the immune complexes and the immunoglobulin molecules (molecular weight 150,000 Daltons).

We have exploited the SEC technique to design a sensor module for the rapid detection of bacteria and other large analytes. Figure 2 illustrates the operation of the module in a specific application involving the detection of pathogenic Salmonella bacteria in a water sample. In this assay, a sample aliquot is first briefly incubated with a concentrated solution of fluorescein-labelled anti-Salmonella antibodies (FITC-Ab). During this reaction, Salmonella bacteria in the sample form immune complexes with the labelled antibodies, and the extent of this reaction reflects the concentration of Salmonella in the sample. The large antigen-antibody complexes are then separated from unbound labelled antibodies by flowing the mixture through an SEC column. As shown in Figure 2, curve B, the bacteria bound to labelled antibodies elute from the column after approximately 8 minutes, while the remaining, unreacted labelled antibodies do not elute until nearly 16 minutes have elapsed. A negative control run, curve A, confirms the 16 minute elution time for fluorescein-labelled antibodies in the absence of bacterial analyte. Positive control runs, not shown in Figure 2, give no fluorescent signal above background at any elution time; this is due to the fact that the bacteria themselves, in the absence of fluorescein-labelled antibodies, are not fluorescent at the detection wavelengths.

The SEC technique is a rapid and convenient means of assaying the results of an immunochemical reaction. It is highly resistant to interferences and false positives, because the early-eluting signal peak appears only when the sample satisfies two criteria simultaneously: the sample must not only react with the specific labelled antibodies, but must also fall within a particular size-dependent window of elution times. Immunologically cross-reacting materials of incorrect size, as well as other bacteria or particulates which are not recognized by the labelled antibodies, do not produce a fluorescent signal peak.

Futhermore, the SEC technique is virtually ideal for repetitive sampling and monitoring applications, because SEC columns are self-clearing. Unlike traditional immunoaffinity columns, where antigens accumulate on an affinity matrix, an SEC column does not saturate with use and does not require replacement or regeneration as some maximum binding capacity is approached. Rather, with an SEC system, both antibody-bound and unbound materials freely flow through and out of the analytical column, and the column may then be reused as soon as the unreacted labelled-antibody peak from the previous assay has cleared the detector. Indeed, the Salmonella sensing module used to produce the data shown in Figure 2 has been used for weeks to assay a variety of positive and negative environmental samples under a range of different conditions. The only constraint was that an interval of at least 30 minutes was required between runs, in order to assure the complete clearance of the labelled-antibody peak from the preceeding assay.

In summary, our protoype integrated immunochemical sensor, incorporating an immunoreaction chamber and an SEC column in tandem, has proven to be a versatile and practical instrument for the rapid detection of large environmental analytes.

OPTICAL FIBER SENSOR MODULE

One alternative to the chromatographic sensor module discussed above is a module incorporating an optical fiber immunosensor. Like the chromatographic sensor, the optical fiber sensor ultimately measures the fluorescence of fluorescein-labelled antibodies. However, unlike the SEC system, the fiber optical system is not subject to significant size constraints on the antigens being detected, and can be used to assay analytes either larger or smaller than an antibody molecule. Also in contrast to the chromatographic module, the optical fiber module does not have a separate immunoreaction chamber. Instead, the immunochemical reaction occurs directly on the surface of the optical fiber sensor.

A schematic diagram of the optical system used in the fiber optic sensing module is shown in Figure 3. In this prototype system designed by ORD, Inc., exciting light is focussed onto the cylindrical end face of an optical fiber. The light propagates within the fiber by total internal reflection, and establishes a narrow evnescent wave zone at the interface between the fiber and the surrounding liquid medium. Fluorescent materials in the liquid phase may be excited by this light in the evanescent wave zone, and the resultant fluorescent emission may then be captured by the fiber and carried by total internal reflection back to the fiber's end face for detection. The excitation and emission maxima of 485 and 530 nm, respectively, are selected to optimize the sensor for the detection of fluorescein. Additional details concerning the instrument design and its principles of operation are available in Reference (1).

In order to adapt this optical fiber sensor for the immunochemical detection of environmental analytes, a sandwich immunoassay configuration is used. Unlabelled capture antibodies are covalently immobilized on the surface of the optical fiber. Brief incubation of an antigen-containing sample aliquot with an immunochemically derivatized fiber results in the selective capture of antigen directly from the sample onto the fiber surface. The quantity of surface-bound antigen is then probed by exposing the fiber to fluorescein-labelled second antibodies. In the absence of analyte, these labelled antibodies exhibit very low nonspecific binding on the surface of an optical fiber bearing only capture antibodies. As a result, few labelled antibodies are brought into the narrow evanescent wave zone at the fiber/liquid interface, and little fluorescent emission is stimulated by the light propagating within the fiber. However, if antigen has been captured from the sample in the previous step, the labelled second antibodies bind with high affinity to the antigens on the fiber surface. The result is a significant fluorescent signal, due to the presence of fluorescein-labelled antibodies within the evanescent wave zone. The intensity of the fluorescent emission correlates with the amount of antigen captured on the fiber surface and, indirectly, with the initial concentration of antigen in the sample.

Using this fiber optic sensor module, a wide variety of molecular and supramolecular analytes may be rapidly and accurately assayed. For the detection of Salmonella typhimurium, results have been obtained which are roughly comparable in sensitivity and response time to those discussed above for the chromatography module. Significantly better performance has been observed for other bacterial analytes, and the fiber optic module has also been successfully employed for the sensitive detection of much smaller molecular analytes. For repetitive sampling applications, a mechanism for fiber replacement is necessary, since efforts to regenerate antibody-coated fibers following antigen binding have proven to be unsatisfactory thus far. However, the flexibility to detect either large or small analytes with a single sensor module makes the integrated optical fiber immunosensor system an attractive choice for many environmental monitoring applications.

SUMMARY

Two integrated immunochemical systems for environmental monitoring have been described, one based upon a chromatographic approach and the other utilizing an optical fiber immunosensor design. The performance of these prototype sensor systems has been illustrated with reference to the immunochemical detection of low levels of bacteria in environmental samples. However, a wide range of analytes, including toxic chemicals and hazardous microorganisms, may be monitored successfully using one or another of the sensors being developed for use with our modular detection systems. Points of distinction have been highlighted which may serve as technical bases for selecting among the various options available in the design of customized immunoreaction/sensor component systems.

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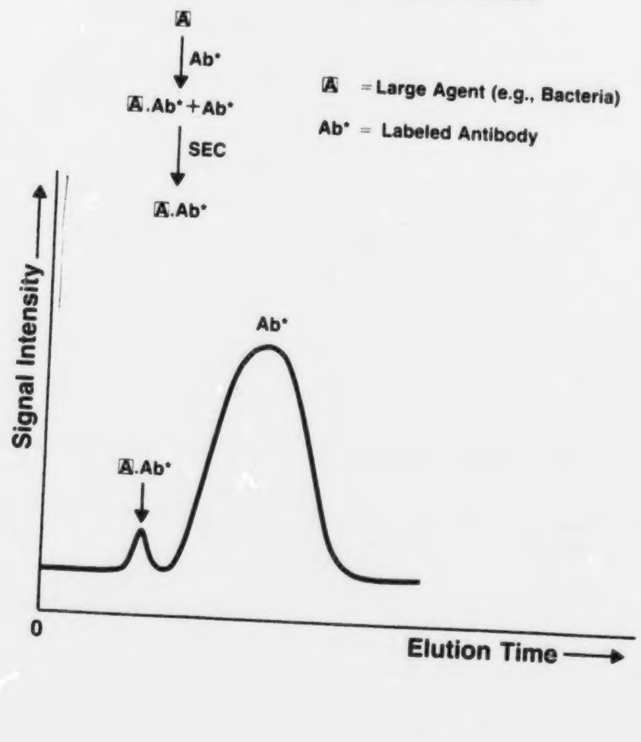
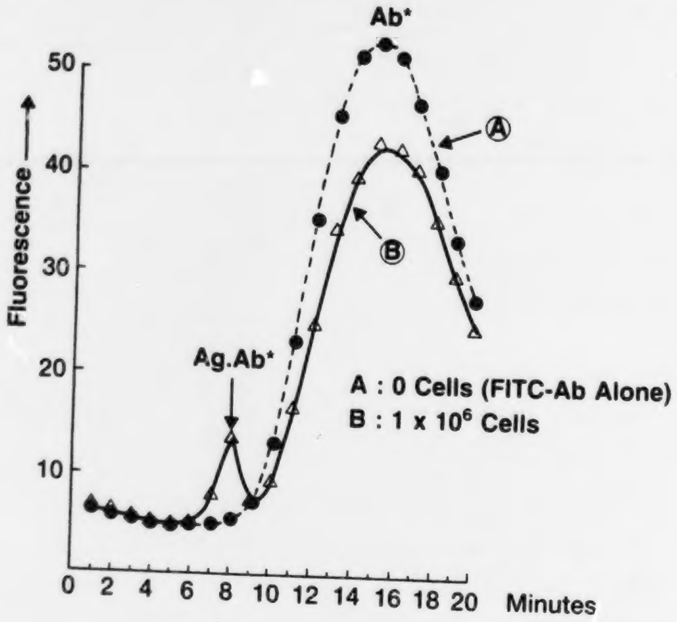
(1) T. Hirschfeld and M. Block, "Assay Apparatus and Methods", United States Patent No. 4,558,014 (12/10/85).

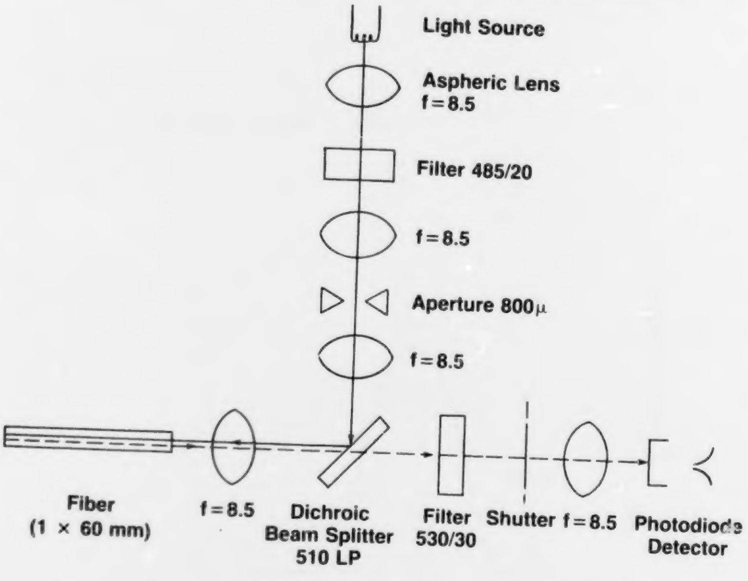
Basic Idea Of The SEC Method



SEC of S. typhimurium



Fiber Optic Waveguide Sensor Optical Schematic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f=8.5
Aperture 800μ
f=8.5
Fiber
(1 × 60 mm)
f=8.5
Dichroic
Beam Splitter
510 LP
Filter
530/30
Shutter
f=8.5
Photodiode
Detector

[Redrawn from ORD User's Manual with permission]

DISCUSSION

BOB HARRISON: You're talking about using a fiber optic weight guide sensor. Could you comment on the regeneration or replacement of the sensor, whether you have disposable sensors and what the implications are for practical field application?

FRANCIS REGINA: For the sensor, we throw the fiber out after one use. The fibers are basically 1 mm by 60 mm.

STEVE GOHEEN: When you immobilized antibodies, did you ever see or experience any problems with winding near the active site with the antibody?

FRANCIS REGINA: No. Generally, we have good activity of our immobilized antibodies.

JEANETTE VAN EMON: How about adapting this to low-molecular-weight compounds, such as environmental contaminants?

FRANCIS REGINA: The size-exclusion chromatography method would be very difficult to adapt to low-molecular-weight compounds, because you need that large analyte that will not be retained in the column to come out with the void volume. If you try to analyze for a protein analyte, you'll basically be trying to separate one protein from a complex of two proteins. In the time frame that we're trying to do it in, using columns that are basically eight or nine centimeters long, with total volumes for the whole column of maybe three or four milliliters, that would be very difficult. The fiber optic wave guide sensor could be very adaptable to small analytes. Protocols wold have to be developed to do competition assays, instead of sandwich assays.

IMMUNOCHEMICAL QUANTIFICATION OF DIOXINS IN INDUSTRIAL CHEMICALS AND SOILS.

Martin Vanderlaan, Bruce Watkins, and Larry Stanker
Lawrence Livermore National Laboratory
Livermore, CA 94550

We have previously reported characteristics of several monoclonal antibodies (Mabs) for the immunoassay of polychlorinated dibenzo-p-dioxins and -furans (PCDD and PCDF; *Toxicology* 45:229) We have applied these to the detection of PCDD and PCDF in a wide range of contaminated samples. For 15 different samples, a direct comparison was made between the levels of PCDD and PCDF contamination determined by conventional gas chromatography-mass spectroscopy (GC/MS) and determined by immunoassay. Samples included fly ash, soil, technical grade chemicals, motor oils, PCB transformer oil, and still bottom residues. These ranged in contamination from less than 1 ppb to several thousand ppb of PCDD and PCDF. The Mabs bind preferentially to tri-, tetra- and penta- PCDD and PCDF containing lateral chlorines, suggesting that they will be well suited for screening samples for the most toxic congeners. The GC/MS data included information on total tetra- and penta- PCDD and PCDF as well as levels of specifically regulated toxic congeners. There was good correlation between the results of the immunoassay and those of conventional GC/MS analysis in spite of these differences in the exact congeners detected by the two different techniques. In general, the immunoassay required substantially less sample clean-up than did GC/MS, thereby offering the promise of substantially reduced costs and time for sample analysis. Sample clean-up consisted of two columns: a carbon column followed by an acid-silica column with dioxin recovery exceeding 70%. Efforts at speeding and automating the clean-up process will be presented.

Funding for this work was provided by the US EPA through Interagency Agreement DW-89931433-01-0 and Hoechst AG. Work was performed under the auspices of the United States Department of Energy by Lawrence Livermore Laboratory under Contract No. W-7405-ENG-48. Chemical samples and GC/MS analysis were provided by Hoechst AG, Frankfurt, FRG.

DISCUSSION

BRUCE MOLHOLT: You mentioned some reconstruction experiments with soil, where you added dioxin and the motor oil back to soil. Did you try that with fly ash to see if you could get 100% recovery of your immunogenecity? With the soil experiments, did you try that over a period of time to see if dioxin binds to soil so that it can't be seen?

MARTIN VANDERLAAN: No. I think we're going to have the same extraction problem that everybody else has. If you're talking about aged New Jersey dioxin in soils, then you probably are going to have to beat on it with a soxlet extractor or something like that to get it out. Immunoassay doesn't solve that problem. It coextracts anything that causes a problem, and it shortens up the overall clean-up procedure a bit.

MARK GREENE: What is the affinity of your antibody for the ligand? Did all of the antibodies that you made for dioxin cross inhibit one another?

MARTIN VANDERLAAN: I haven't done the cross inhibition check. My assumption is that with a small molecular weight like this, you really can only put one antibody on a molecule and that once it's bound, nothing else will bind it. But that's an assumption I haven't tested.

I also haven't measured the exact affinity constant, because that's fairly tricky for something that isn't water soluble. To get these assays to work, you've got to use a little detergent. And the dioxin is probably sitting in detergent micelles. You could make measurements, but I'm not sure what they would mean. I feel much more comfortable reporting the sensitivity of the assay and the performance of the assay. That's the measure that is of greatest value. I think that that is related to antibody affinity, but it isn't a strict quantitative measurement.

JEANETTE VAN EMON: Can you describe in small detail your sample preparation?

MARTIN VANDERLAAN: We will extract the sample by whatever means you like. If it's a case of fly ash, it was treated with acid and then soxlet extracted. If it's the case of soils, we mix it with sodium sulfate and then shake it in hexane for half an hour or so, with a couple of changes of hexane.

Once the sample is extracted, it's run over a carbon column. There are a couple of washes of solvents there where other things wash through. Then it's diluted in toluene. We then mix that with acid-impregnated silica and dry that down onto the silica, so we're doing a sulfuric acid treatment on a solid-phase silica matrix. We pour hexane over that, and the dioxin comes off because it didn't react. That gets dried down into a little bit of detergent and resuspended with the antibodies.

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REMOTE, CONTINUOUS, MULTICHANNEL BIOCHEMICAL SENSORS BASED OF FLUOROIMMUNOASSAY TECHNOLOGIES

J-N Lin, P. Kopeckova, J. Ives, H. Chuang, J. Kopecek*, J. Herron, H-R Yen, D. Christensen, J.D. Andrade*
Department of Bioengineering
University of Utah
Salt Lake City, UT 84112, U.S.A.
*Institute for Macromolecular Chemistry
Prague 6, Czechoslovakia

The advances in fluoroimmunoassay, coupled with the rapid development of fiber optics, planar waveguides, and integrated optics, make it feasible to construct and apply remote, continuous multichannel biochemical sensors. The development of such immunosensors requires: a) preparation, characterization, selection, and immobilization of the needed antibodies or antibody fragments; b) a means to deliver remotely the fluor or fluorescently-labelled competing Ag; c) a means to regulate the Ag-Ab binding properties to allow reasonable response times or externally controlled "zeroing" of the sensor; d) an inexpensive and reliable means to excite fluorescence with minimal excitation of general background fluorescence; e) a convenient means of detecting, collecting, and processing the emitted fluorescence so as to obtain a quantitative assay; f) means to provide many sensing channels to permit the assay of 2 or more analytes together with the needed reference and blank channels.

We are addressing all of these problems in a coordinated fluorosensor development program. Progress on each of the component areas will be briefly discussed using results from prototype sensors for prothrombin and antithrombin III.

DISCUSSION

MEL SWANSON: You stated that for covalent immobilization to occur, an antibody has to adsorb first. Would that be true only of hydrophobic surfaces, or would it also be true of hydrophilic surfaces?

JOE ANDRADE: It's got to get there first, and it has to have a residence time there greater than a thermal fluctuation. And that means basically an adsorption event. That adsorption event and the covalent immobilization can occur almost simultaneously, but it's unlikely, because it's coming up to the surface.

There is a repertoire of functional groups on the surface of a protein – the amino groups that are used to covalently immobilize it (sulfhydryl, etc.) There is also a whole array of nonpolar groups on most protein surfaces – so-called hydrophobic patches. On a hydrophobic surface, the protein which is the most tightly adsorbed is certainly adsorbing through the face with the greatest hydrophobic character. There's a whole variety of collision events and processes going on. You must imagine the protein interacting with the surface, colliding with that surface through all possible orientations. Some of those orientations essentially lead to no residence time or just diffusion-limited residence time. Other orientations lead to a substantial residence time. Those orientations are not necessarily the same orientations required for covalent immobilization. After the abdsorption event, the thing diffuses around on the surface and partially denatures. And in that squirming on the surface, which takes on the order of seconds to minutes to even longer, it finally finds a reactor group. And then the reactive event may occur. The adsorption event is critical to the immobilization event in most systems.

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A Microbial Bioassay Developed for Rapid Field Screening of Hazardous Waste Sites

I. Cecil Felkner, Ph.D.
Tom Christison, M.T.

Brenda Worthy, M.T.
Christine F. Chaisson, Ph.D.

ABSTRACT

A laser/microbial bioassay technology that is cost effective, accurate, and quantitative for various classes of chemical toxicants present in the environment has been developed. This system is capable of identifying and quantifying toxicants in various matrices which are likely to contain the environmental pollutants on the U.S. Environmental Protection Agency´s priority list, even when these substances are present at low levels. The system has the significant advantage of being field portable, rapid, and sensitive while still incorporating a high level of specificity for numerous toxic chemicals and chemical classes. Furthermore, the system is capable of distinguishing between those substances that possess cytotoxicity only and those which have genotoxic properties; hence the potential for identifying those which might produce acute toxic symptoms but possibly chronic disease, e.g., cancer, as a consequence of chronic exposure at low levels. The bioassay system consists of a laser photometer that makes 1200 measurements/second at 15 unique angles over a 180 degree arc and an isogenic set of Bacillus subtilis mutants. The laser detects toxicity to the bacteria (in a liquid sampling cuvette) by differential light scattering (DLS) of a fine beam which is measured quantitatively in terms of intensity at the various angles. The parameters recorded are the number of bacteria, their size, shape and distribution, and any increases or decreases in all of these parameters. The quantitative determination of toxicant concentration is a function of the dose-response kinetics by the bacteria in a given sample; the specificity of response to a given chemical/chemical class is made possible by monitoring bacterial mutants that differ from each other by only one property, which causes them to be more sensitive than the other set members based on the mechanism of toxicity. Therefore, a "fingerprint" unique to each chemical can be generated from the differential response of the 19-member test set of bacteria. Since the system also includes a metabolic activation capability in a unique "solvent" cocktail, carcinogenic chemicals such as benzo(a)pyrene and dimethyl hydrazine are easily identified and quantified. Finally, individual samples can be read and analyzed by an integrated computerized system so that 5 to 10 concentrations of an aqueous sample can be processed in just over one hour.

INTRODUCTION

Instrumentation and methods used in environmental monitoring have typically been those from analytical chemistry for assaying chemical residues. This has been for a very good reason -- the availability of numerous, specific chemistry-based methods that have been validated by well-established academic, federal, state, and private institute laboratories who are frequently called upon to perform analyses in a rather large variety of matrices, e.g., water, soil, air, and food. In fact, the United States Environmental Protection Agency (USEPA) set forth the "Guidelines Establishing Test Procedures for the Analysis of Pollutants," (FR 44:No.233, 1979, under 40 CFR Part 136), in which methods such as gas chromatography (GC), high performance liquid chromatography (HPLC), mass spectroscopy (MS) and inductively coupled plasma optical emission spectroscopy (ICP) were listed as the acceptable analytical procedures for organic and inorganic analyses. These methods are highly reliable when linked with the appropriate extraction methods, compound-specific reactions, and suitable detectors. However, these analytical procedures do not provide, and are not intended to provide, a direct assessment of the toxicity of chemical residues. Also, unique procedures must be developed for each chemical or chemical class; performance of these conventional analytical procedures destroys the sample because the method usually entails such

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preparatory steps as extraction, chemical treatments to facilitate separation of the sought components, and chemical conversions to generate the detectable chemical species. By necessity, analytical laboratories are geographically fixed, making it necessary to store and transport samples and thereby create a holding time. During the holding time, it is expected that problems for the analyses will be created, particularly when the sample materials are volatile, bind to the container (e.g., the pesticides paraquat and diquat stick to glass or borosilicate containers),or can degrade under the conditions of storage and transportation. Finally, it is expensive to use traditional analytical methods because they require sophisticated instrumentation, highly purified solvents and gases, frequent equipment standardization, and highly trained technical professionals.

In view of the requirements and attendant resource expenditures cited above, there is a serious problem created for truly adequate monitoring of the environment for toxicants. Felkner, et al. (1988) have noted the need for "cheaper, quicker, and more sensitive analytical methods for detection of chemicals in the media in which the chemicals may exist," and have emphasized that such needs are recognized by Congress, regulatory agencies, consumer advocates, scientific societies, private industry, and other segments of society. Corporations and/or collaborating federal agencies involved in toxic site cleanup are burdened with expensive and time-consuming analytical methods to determine the extent to which a cleanup is effective. Moreover, these procedures do not benefit from rapid and inexpensive prescreening technology and must therefore be used to analyze all of the collected samples until a statistically representative sample size has been reached; hence, there will be numerous analyses performed on samples lacking the toxicants being sought (in fact, the vast majority of samples are negative) at great expense to those who must finance this monitoring. This optimizes the chance that humans will be exposed to harmful levels of toxicants, and the lack of adequate monitoring may also prevent the further development and use of potentially beneficial chemicals, not due to the health risk but because methods to quantify their residues in food, water, or soil may not exist or may be too costly to warrant their development.

New technological approaches that offer inexpensive and efficient ways to screen for toxicants in the environment are needed, but any developed system must have adequate sensitivity and specificity and should be portable, ideally capable of collecting and quickly analyzing samples on site. This capability exists for the laser/microbial bioassay system which is described in this paper as a candidate for further development as an on-site system for monitoring toxic waste cleanup.

METHODS

The laser/microbe bioassay system developed by Felkner, et al. (1988) has been described in detail in the published literature. Briefly, it is a 66 min. computerized bioassay that utilizes 19 isogenic strains of Bacillus subtilis to characterize and quantify the toxicants present in an aqueous solution. The response of the bacteria to toxic substances is monitored by differential light scattering from a laser beam (632.8 nm), which is received by an array of detectors and input directly into a microcomputer that analyzes the toxic response through developed software programs. A fingerprint, generated from the members of the isogenic set of bacteria, specifies the identity of a given toxicant based on its mechanism of action (i.e., a biological detection that relates the structure of the chemical to its activity). The entire assay is accomplished by incubating the test sample with the bacteria in a small vial that is heated by a heating block at 37 C; specifically, a small pellet of the tester bacteria with lyophyllized media is added directly to the vial containing distilled water after which the sample increment is also added. Details of the assay performance are given below.

The bioassay is performed with or without metabolic activation. For the nonactivated assay, lyophilized bacteria-media (sufficient Brain-Heart Infusion [BHI] broth to support the growth of the bacteria during the assay) are introduced into the incubation cuvette (scintillation vial) containing 1.0 ml of deionized water and mixed, held at 60C for 8 min., further diluted with 4 ml of water and then incubated at 37 C until an assay-ready stage is reached (when this culture can be diluted 1:20 and yield a concentration of 10^6 bacteria/ml). A computer program recognizes this stage, at which time the assay or control (+/-) sample aliquot (0.1 ml in 10ml of distilled water) may be added. The negative control culture is required to have an acceptable generation time (e.g., approximately 40 min. for the wild type strain or a doubling time of 27.6 min.) before an assay is considered valid. Readings are taken at 0, 6, and 66 min., respectively, to determine growth inhibition and/or any changes in shape or size of cells (relative to the control culture) as a measure of toxic response.

These measured responses are dose-related and therefore quantitative for the toxicant concentration.

For metabolic activation, 0.5 ml of S9 mix (microsomal fraction at 30 mg protein/ml) is added to the solubilizer (cocktail contains emulsifier-dispersant) at the time the assay sample is added. All other conditions of the assay are the same as in the nonactivated assay. However, it should be noted that although the cocktail components have no effect on bacterial growth, they facilitate delivery of water insoluble compounds to the detector bacteria; hence, it can be used for assays with or without S9 mix.

Specific software programs have been designed to analyze the assay responses (Felkner, et al., 1988) to determine how toxicants affect the various members of bacterial isogenic sets (isosets). By exposing the bacterial cultures of these isosets to varying dilutions of the test material and including a non-dosed control, concentration dependent effects can be assessed. Any differences between strain responses are scored and recorded, thus becoming a response profile for the assayed material. If differential sensitivity is seen between any members of the 19 B. subtilis strains, the test material is judged as genotoxic, otherwise, any toxicity measured is considered to be cytotoxicity and not likely to have chronic effects such as the potential for carcinogenicity. In addition, the responses can be analyzed to show the mechanism(s) by which toxicity is exerted, the structure-function relationship through which the system is able to specifically identify chemicals. All data are also analyzed statistically and carried through data reduction procedures leading to data printout for each assay.

RESULTS

The data which follow are not intended to be exhaustive, but should serve to illustrate the systems's capability for detecting toxicants in the environment. Hence, an example of a toxicant which does not require metabolic activation, 4-nitroquinoline-1-oxide (4NQO) and one which requires metabolic activation, benzo(a)pyrene (BAP) are presented. In the five figures, the profiles of the test bacteria are generated by a plot of the relative intensity of scattered light (y axis) versus the scattering angle (x axis) at which the detectors received the light beam scattered by the bacteria (particles). Increases in intensity show increases in the number of bacteria (growth) and a shift in the profile to the smaller scattering angles indicates that the bacteria are increasing in size (swelling) whereas a shift in profile to the larger scattering angles indicate a size decrease (shrinking). From increases on the y axis, the number of bacteria are calculated, so that N_0 represents the bacteria present at 0 time and N represents the bacteria present after 66 min. of incubation for either the negative control or a sample dosed at a given concentration. Hence N/N_0 represents the relative increase in bacteria from which the generation time (TAU) can be calculated, and TAU/TAUC represents the generation time of a dosed sample relative to the control. Thus, an increase in TAU/TAUC represents growth inhibition, a decrease means growth stimulation, and a value of 1.0 means there is no effect by the treatment.

Figure 1_a represents the normal growth of a tester strain (strain 10 or B. subtilis strain fh2006-7) which has an N/N_0 of 5.2 and a TAU of 40.06 min. Figure 1_b shows the same strain that has been dosed with 0.15ug/ml of 4NQO for which N/N_0 was reduced to 2.1 and TAU is 90.94 min. Figure 1_c is a combination of the data from Figures 1_a and 1_b which can be compared so that TAU/TAUC can be calculated. In this case the values are 1.0 for the control and 2.27 for the sample treated with 0.15 ug/ml of 4NQO. The TAU/TAUC values for 0.15,1.5, and 4.5ug/ml of 4NQO were determined to be 2.27, 3.35, and 11.50, respectively, showing that the generation time is increased in a dose-responsive manner and that TAU/TAUC corresponds directly to a specific dose for a specific strain.

Figure 2 represents the response of strain 11 (wild type or normal strain) to 7.6 ug/ml BAP. Here, TAU for the control was 46 min. and the TAU/TAUC value was calculated as 1.14. Figure 3 represents the response of strain 19, a mutant strain that specifically cannot repair the type of damage caused by the BAP metabolite produced by S9 activation. The TAU for the control was 48 min. and the TAU/TAUC was 2.27. This data shows that metabolized BAP has a greater effect on the mutant than the wild type strain and that BAP has an adverse genetic (genotoxic) effect. The TAU/TAUC value for strains 11 and 19 at BAP concentrations of 15.1 ug/ml in the presence of S9 activation were 2.15 and 2.59, respectively which showed that at this increased concentration even the wild strain was damaged and that the effect on the mutant was increased further.

SUMMARY AND CONCLUSIONS

The data presented here, though abbreviated, show that the laser/microbial bioassay system can detect a toxic response from chemicals that are directly toxic (4NQO) or those that require metabolic activation (BAP). The total assay time is 66 min., and the data are collected and stored on software immediately when the samples are assayed by the laser through differential light scattering. The response can be directly correlated with the dose by calculating the effect of the test chemical on the rate of growth (generation time or TAU). The calculations are done automatically by this computerized system within a matter of seconds. The system is not dependent upon a separate assay for each chemical or chemical class but depends upon response of the mutants based on the mechanism by which each chemical exerts its toxicity. Therefore, the response is specific and moreover quantitative when related to the dose response. Finally, the system can be made field portable and further developed for on-site toxic waste cleanup monitoring.

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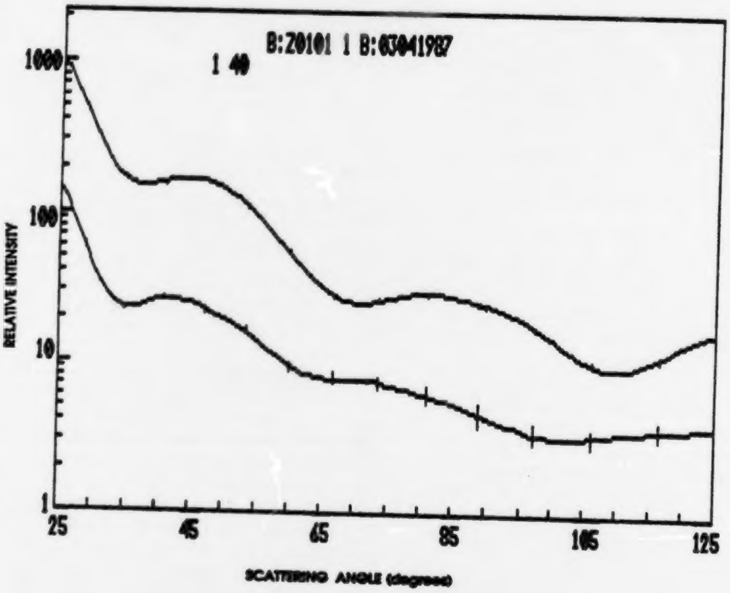


Figure 1a. Growth of untreated control culture of Bacillus subtilis strain fh2006-7 (No. 10) monitored by laser differential light scattering and scored for generation time (TAU).

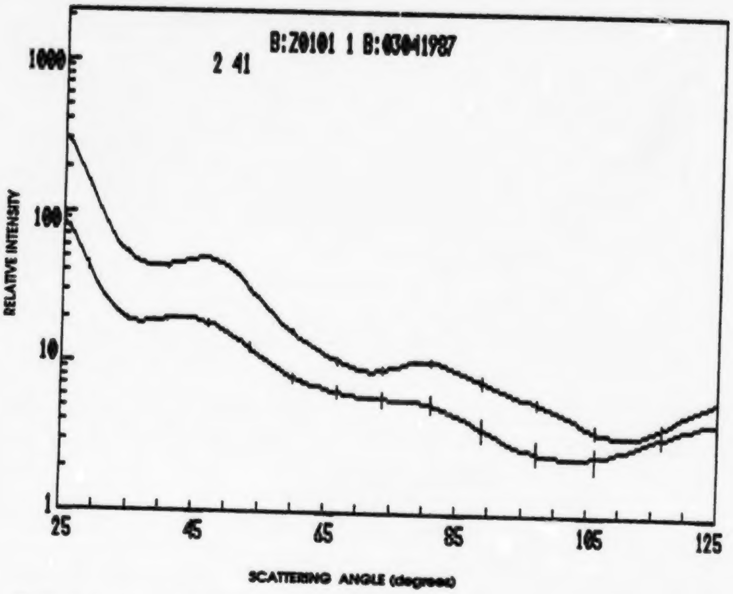
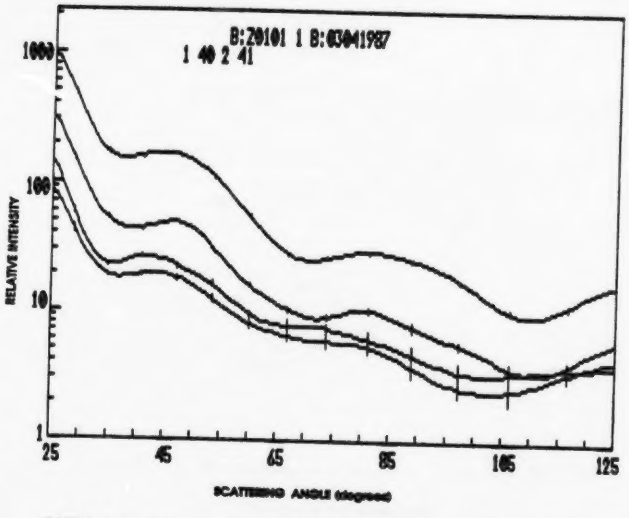


Figure 1b. **Growth of <u>Bacillus</u> <u>subtilis</u> strain fh2006-7 treated with 0.15 ug/ml of 4-nitroquinoline-1-oxide monitored by laser differential light scattering and scored for generation time (TAU).**



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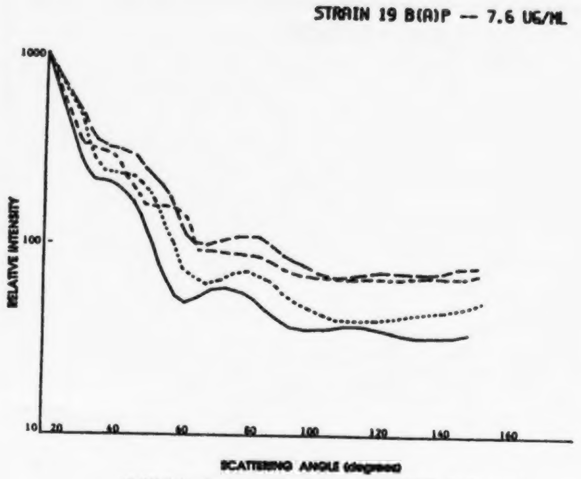
        SCORING FILES FOR 4-NITROQUINOLINE-1-OXIDE DATA (1a,1b,1c)

SMP   SET#        TIME(m)    N/NO        TAU       TAU/TAUC   STR   CONC*
1      1 40       66MIN      5.2        40.06      1.00       10    0.00
2      2 41       66MIN      2.1        90.34      2.27       10    0.15
3      3 42       66MIN      1.6       134.15      3.35       10    1.50
4      4 43       66MIN      1.2       463.71     11.50       10    4.50
*ug/ml
```

Figure Ic. **Comparison of <u>Bacillus</u> <u>subtilis</u> strain fh2006-7 control culture to culture treated with 0.15 ug/ml of 4-nitroquinoline-1-oxide by scoring the TAU/TAUC ratio as related to dose. 4NQO concentrations of 1.5 and 4.5 ug/ml are scored but not shown graphically.**

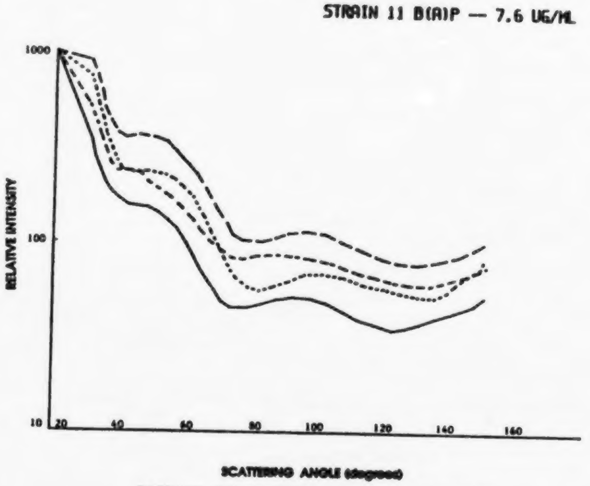


SCORING FILES FOR BENZO(A)PYRENE DATA (3)

SMP	SET#	TIME	TAU	TAU/TAUC	STR	CONC*
4	7 10	66MIN	48.03	1.00	19	0.00
5	8 11	66MIN	109.03	2.27	19	7.60
6	9 12	66MIN	124.40	2.59	19	15.1

*ug/ml

Figure 3. **Comparison of Bacillus subtilis polA101.his.met (strain 19) growth in the presence and absence of 7.6 ug/ml BAP metabolically activated with a microsomal fraction (S9) using differential light scattering and scoring for TAU/TAUC. Treatment with 15.1 ug/ml of BAP is also scored but not presented graphically.**



SCORING FILES FOR BENZO(A)PYRENE DATA (2)

SMP	SET#	TIME	TAU	TAU/TAUC	STR	CONC*
1	1 5	66MIN	46.01	1.00	11	0.00
2	2 4	66MIN	52.45	1.14	11	7.6
3	3 6	66MIN	99.12	2.15	11	15.1

*ug/ml

Figure 2. **Comparison of Bacillus subtilis wild type strain (No. 10) growth in the presence and absence of 7.6 ug/ml benzo(a)pyrene (BAP) metabolically activated by a microsomal fraction (S9) using differential light scattering and scoring for TAU/TAUC. Treatment with 15.1 ug/ml of BAP is also scored but not presented graphically.**

DISCUSSION

JEANETTE VAN EMON: About how long does it take to screen a panel for mutants for a particular compound?

CECIL FELKNER: It takes probably whatever the time is (a morning, half a morning, or something like that) once the primary screen to determine the profile is made.

Sometimes you're surprised, and the response is so great that everything is wiped out. You then dilute until you get an appropriate level and redo the process.

What you're doing takes really about an hour of your time. The computer and the software programs process this immediately. Then you would have the profile for quantitative determination of the concentrations.

We are beginning to build libraries relative to various chemicals. If you're dealing with nice, clean chemicals, there shouldn't be any problem. But what happens if you have a real-world situation? One of the early things that we had to do with this bioassay was to be able to detect toxicants in the face of confusants, such things as bentonite, pH differences, and so forth. We had 11 to 15 different types of confusants that were put in the presence of the toxicants for which we had to make specific identification. This was a successful operation.

Monitoring Volatile Organics in Water by a Photovac Portable Gas Chromatograph with Multiple Headspace Extraction Method

James S.Ho
Paul Hodakievic*
Joseph F. Roesler

Environmental Monitoring and
Support Laboratory
U.S. Environmental Protection Agency
26 W. Martin Luther King Dr.
Cincinnati, Ohio 45268

* Technology Applications, Inc.
c/o Environmental Monitoring &
Support Laboratory
U.S.Environmental Protection Agency
26 W. Martin Luther King Dr.
Cincinnati, Ohio 45268

ABSTRACT

A Photovac 10S50 portable gas chromatograph equipped with a capillary column and a photoionization detector (10.6 eV) in conjunction with a head space sampling device is evaluated for monitoring volatile organics in water. A multiple headspace extraction technique is described for quantitative determination of volatile organics in water samples of various matrices. This method, first proposed by McAuliffe, consists of a repeated analysis of vapor over liquid after replacing the analyzed equilibrated gas by an equal volume of pure air with its subsequent equilibrium. The advantage of this method is that it simultaneously determines contents in the equilibrium gas and also measures the partition coefficients (K) for the liquid sample under investigation. This method eliminates the influence of a sample matrix on the phase equilibrium. Therefore, it can determine volatile organics in all types of aqueous samples without prior standardization and without concern for a potential matrix effect from complex constituents found in samples of hazardous waste sites.

INTRODUCTION

Portable field instruments for monitoring and screening at hazardous waste sites are expected to be used widely for both quantitative and qualitative determination of volatile and semivolatile organic contaminants in air, water and soil. As a screening tool, portable monitors minimize the time and expense associated with transporting uncontaminated samples back to the laboratory for analysis. Moreover, the on-site analytical instrument provides immediate results by which prompt and appropriate sampling, off-site analyses and corrective action may be undertaken.

A 1985 study involving 183 hazardous waste disposal facilities demonstrated that volatile organics were detected more frequently than other types of priority pollutants in groundwater (1). This finding suggested that volatile organic scans might be used as a screening technique to establish the extent of organic contamination of hazardous waste sites. One of the instruments, the Photovac portable Photoionization detector (PID) gas chromatograph, which has been widely used as a monitor for toxic organic vapors in ambient air, may be used for analyzing the water samples from hazardous waste sites.

This paper discusses the use of the Photovac 10S50 portable gas chromatograph with a capillary column and a photoionization detector (10.6 eV.) in conjunction with a multiple headspace extraction (MHE) technique for quantitative analysis of volatile organics in water.

THEORETICAL PRINCIPLE OF THE MULTIPLE HEADSPACE EXTRACTION (MHE) TECHNIQUE

MHE was first proposed by McAuliffe (2,3) to determine the solubility of hydrocarbons in water. Steps of MHE are depicted schematically in Figure 1. First, a volume of sample solution is placed into a calibrated glass syringe followed by a volume of clean air (headspace). During the equilibration period between the liquid sample of volume V_L and the gas that occupies volume V_G, a portion of volatile compound in the liquid will partition into the gas phase. The phase distribution of the analyte is defined by a mass balance equation:

$$C_L V_L = C_L V_L + C_G V_G \qquad (1)$$

where C_L is the initial analyte concentration in the liquid, and C_L and C_G are the equilibrium concentrations in

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the liquid and gas phases respectively. Applying the distribution law, $C_L = KC_G$, where K is the partition coefficient for the compound in question, the equation above may be substituted and rearranged to yield the following relation:

$$C_L = C_G(K+V_G/V_L) \qquad (2)$$

After equilibration, the gas chromatographic determination of C_G is conducted, and then the equilibrated gas is completely expelled from the syringe and replaced with a fresh volume of air. The remaining quantity of analyte in solution (V_LC_L) redistributes between the two phases. GC analysis is then performed on the replacement air. This pattern may be iterated any number of times.

The formula for the determination of volatile organics in solution utilizing multiple headspace extraction under static conditions and with equal volume of V_G and V_L can be derived from equation (2):

First extraction

$$C_L = C_{G1}(K+1) \qquad (3)$$

Second extraction

$$C_L = C_{G2}(K+1)^2/K \qquad (4)$$

nth extraction

$$C_L = C_{Gn}(K+1)^n/K^{n-1} \qquad (5)$$

and

$$C_{Gn} = K^{n-1}C_L/(K+1)^n$$

$$= (C_L/K)/(1/K+1)^n \qquad (6)$$

$$\mathrm{Log}C_{Gn} = \mathrm{Log}(C_L/K) - n\mathrm{Log}(1/K+1) \qquad (7)$$

A semilog plot of C_{Gn} VS n is a linear relationship with the slope being a function of K only and the intercept being a function of initial sample concentration, C_L, and K.

MATERIALS AND METHODS

Gas Chromatograph

The GC used for this analysis was a portable Photovac Model 10S50 with a PID detector(10.6 eV.). It was equipped with a 0.53 millimeter X 10 meter encapsuled capillary column coated with 100% chemically bonded dimethylpolysiloxane (Photovac Inc.) . Synthetic pure air was used as the carrier gas and supplied at a pressure of 40 psi. The column flow was set to 4.3 ml/minute. Since the Photovac is not equipped with an oven, the column temperature was not controlled. For this reason the column temperature fluctuated but usually stayed in the range of 32-42 degrees Celsius.

Instrument Evaluation

In order to show that the Photovac is a dependable instrument a gas phase standard was analyzed five times and the precision of the analyses calculated. The results are reported in Table 1. Figure 2 shows a typical chromatogram of the six volatile organics. Detailed evaluations(4,5) have shown the Photovac to be an effective and handy portable GC. The six volatile organics chosen for this study are trichloroethylene, benzene, 1,1,1-trichloroethane, chloroform, 1,1-dichloroethane, and methylene chloride. These chemicals were chosen because they represent some of the more common pollutants found at contaminated ground water sites(1).

Calibration vapor phase standards were made by injecting a standard mix of the volatiles in methanol into a sealed glass flask. The flask was then allowed to sit for half an hour before it was analyzed by the GC. The three point calibration curves generated were linear as evidenced in Figure 3A and 3B.

Multiple Headspace Extraction (MHE) Technique

Three different sample matrixes, 5% NaCl, 10% Nacl, and primary waste water effluent from the City of Cincinnati's sewage treatment plant were studied. The salt solutions were chosen to represent the effect ionic strength had on the phase equilibrium of the volatiles. To perform the MHE, the liquid sample is poured into a 100 ml gas-tight syringe filling it to the brim. The plunger is then pushed to remove all but 50 ml of the sample. The calibration standard mix is injected into the syringe and the syringe is immediately sealed. The syringe is allowed to sit for 30 seconds after which 50 ml of room air is drawn into the syringe. The sample is then mildly shaken for 30 seconds and allowed to sit for 10 minutes. After 10 minutes, equilibration is reached and the sample is analyzed by the GC. The Photovac has an internal pump which draws a headspace sample into a sample loop. The sample in the loop is flushed into a precolumn and column. The amount of sample entering the column is determined by the carrier gas flow rate and the time that the valves joining the loop and columns are left open. During the time that the sample is being drawn into the GC a partial vacuum is created in the 50 ml syringe headspace interfering with the sample flow. This problem is avoided by pushing the syringe barrel up at the same time that the sample is being taken. Care must be taken to avoid drawing any water into the system. After the first sample is taken, the remaining air in the syringe is pushed out and 50 ml of new air drawn in. The sample is then shaken and analyzed as before. This process is repeated until the desired amount of extractions are analyzed.

Calculations

The peak area for each compound is plotted on semilog paper for each extraction. Figure 4 shows the results of six volatiles spiked in reagent water which underwent five iterative extractions. The y-axis intercept is found by drawing the best fit line between the points and is equal to C_L/K (Equation 7). K is equal to the reciprocal of the slope minus 1. A sample calculation for one of the six volatile analytes, 1,1-dichloroethane, may be summarized as follows:

y-axis intercept = 9.1

based on the three point calibration curve for 1,1-dichloroethane and a response of 9.0 the y-axis intercept concentration, C_L/K = 352 ug/L

slope = 1.2

$K = 1/(1.2-1) = 5.0$
$C_L = 352$ ug/L * 5.0 = 1762 ug/L

The true value for C_L was 1753 ug/L. The discrepancy between the known concentration and the measured concentration using the above procedure was 0.5%.

Liquid Standard Technique

The more common technique for headspace analysis is to perform just one extraction and compare the peak areas to a liquid standard. Reagent water was spiked at the same concentration as the samples and the first extraction peak areas were used for calculating the original concentration of the volatiles in the samples.

RESULTS

Table 2 lists and compares the results of the MHE and liquid standard techniques. Figure 5 shows this comparison in graphical form. These results show that the MHE provided much greater accuracy than the liquid standard technique. The discrepancy range for the MHE method was from -20.1 ±11.2 % for dichloromethane in waste water to +29.7 ± 15.5 % for chloroform in 10 % NaCl solution as compared to the discrepancy range for the liquid standard technique which was -64.2 ±20.1 % for trichloroethylene in waste water to 167.3 ±49.0 % for trichloroethylene in 10 % NaCl solution.

Table 3 lists the K values found for the six compounds in the three matrixes and reagent water. The difference in K values between the 5% and 10% NaCl and reagent water explains the much greater discrepancy of results when using the liquid standard technique for these matrixes. The K values for the waste water are not greatly different from those of the reagent water, but the accuracy still suffered when using the liquid standard technique in waste water. This points out another advantage of the MHE method; several extractions are performed, and if one of the extractions is off, that point may be discarded. In the case of the waste water, the first extraction peak areas were low compared to the subsequent extractions, due most likely to spurious adsorption effects similar to those reported by Drozd(6). Using the MHE technique on the water, the first extraction point could be discarded and still sufficient data would remain for an accurate determination of C_L and K. The liquid standard method, however, lives and dies on the first extraction; a definite disadvantage, especially when the quantity of sample is limited.

CONCLUSIONS

The above examples have shown how volatile organic compounds in water samples of various matrices can be quantitatively analyzed with the MHE procedure. The major advantages of using the Photovac 10S50 portable GC with the multiple headspace extraction method are:

1. More accurate data can be obtained by using the MHE procedure in comparison with the standard single extraction liquid standard procedure.

2. Use of this technique for on-the-spot analysis reduces the cost of sending unnecessary samples back to the laboratory for analysis. Quick decisions can also be made to redirect investigations of hazardous waste sites.

3. With the MHE method, the influence of a sample matrix on the phase equilibrium is eliminated. It simultaneously determines the analyte contents in the equilibrium gas of a headspace and measures the partition coefficient (K) for the liquid sample under investigation. Therefore, a Photovac portable GC combined with the MHE technique provides a useful field ability to determine volatile organics in all types of aqueous samples. It requires no external aqueous calibration standard and has no need for concern about matrix effects which are likely to occur in complex samples found at hazardous waste sites.

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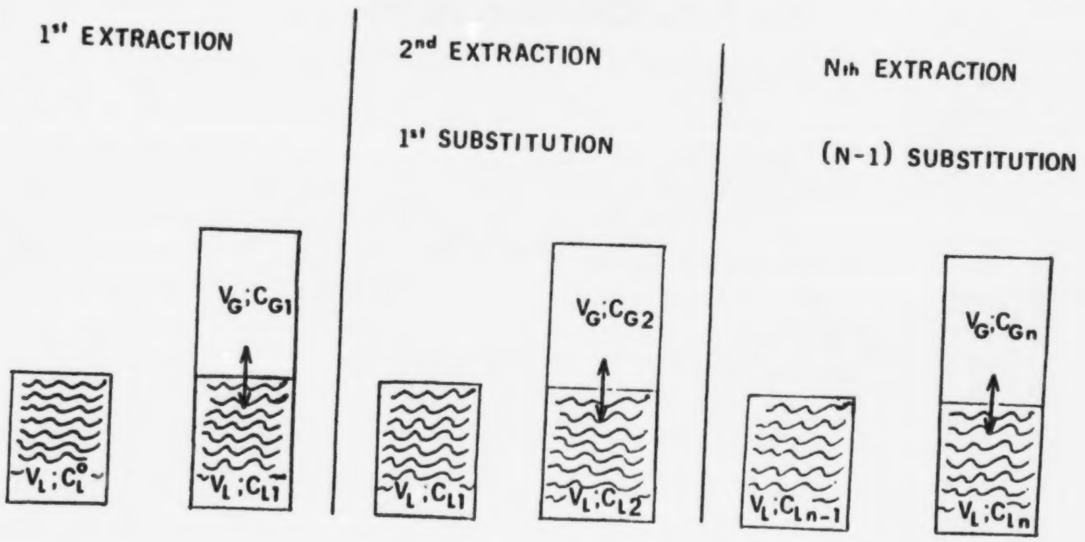

1st EXTRACTION
2nd EXTRACTION
1st SUBSTITUTION
Nth EXTRACTION
(N-1) SUBSTITUTION
$V_G; C_{G1}$
$V_L; C_L^0$
$V_L; C_{L1}$
$V_G; C_{G2}$
$V_L; C_{L1}$
$V_L; C_{L2}$
$V_G; C_{Gn}$
$V_L; C_{Ln-1}$
$V_L; C_{Ln}$

FIGURE 1. DIAGRAM OF MUTIPLE HEADSPACE EXTRACTION

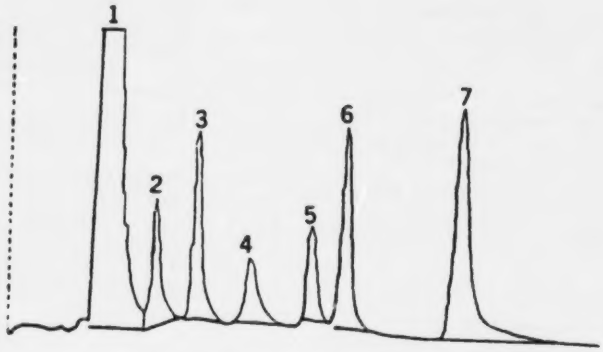

Figure 2. Typical chromatogram of the six volatile organics. Peak 1 is the solvent peak. The other peaks are as follows: 2. methylene chloride 3. 1,1-dichloroethane 4. chloroform 5. 1,1,1-trichloroethane 6.benzene 7. trichloroethylene.

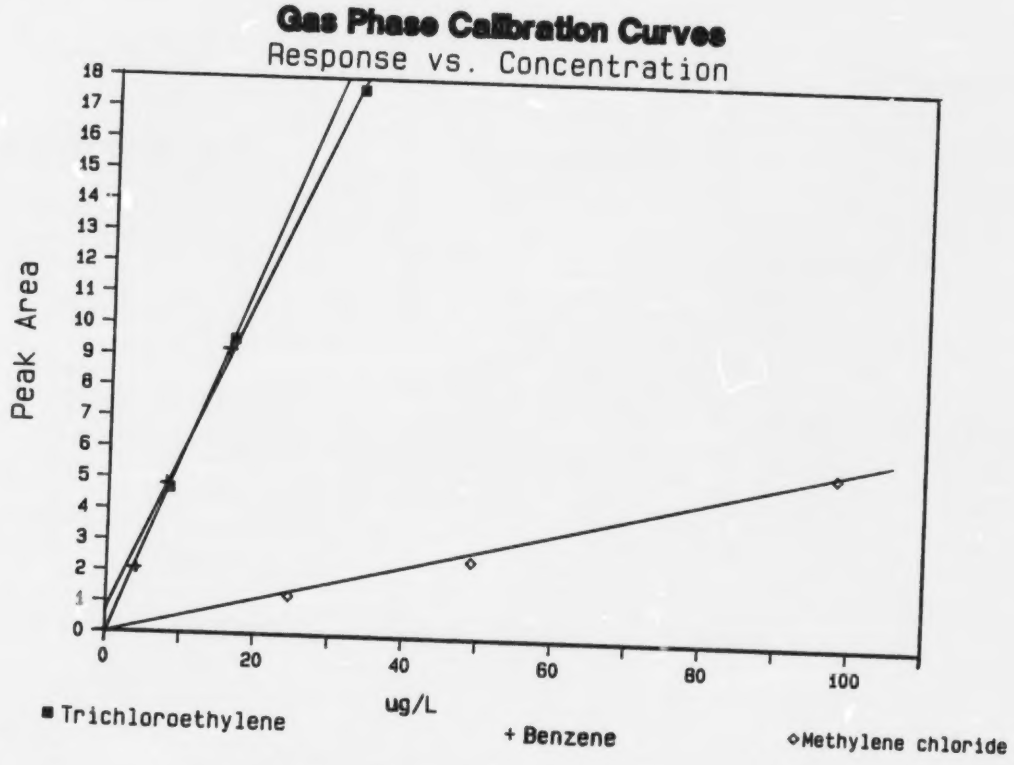

FIGURE 3A. THREE POINT CALIBRATION CURVES

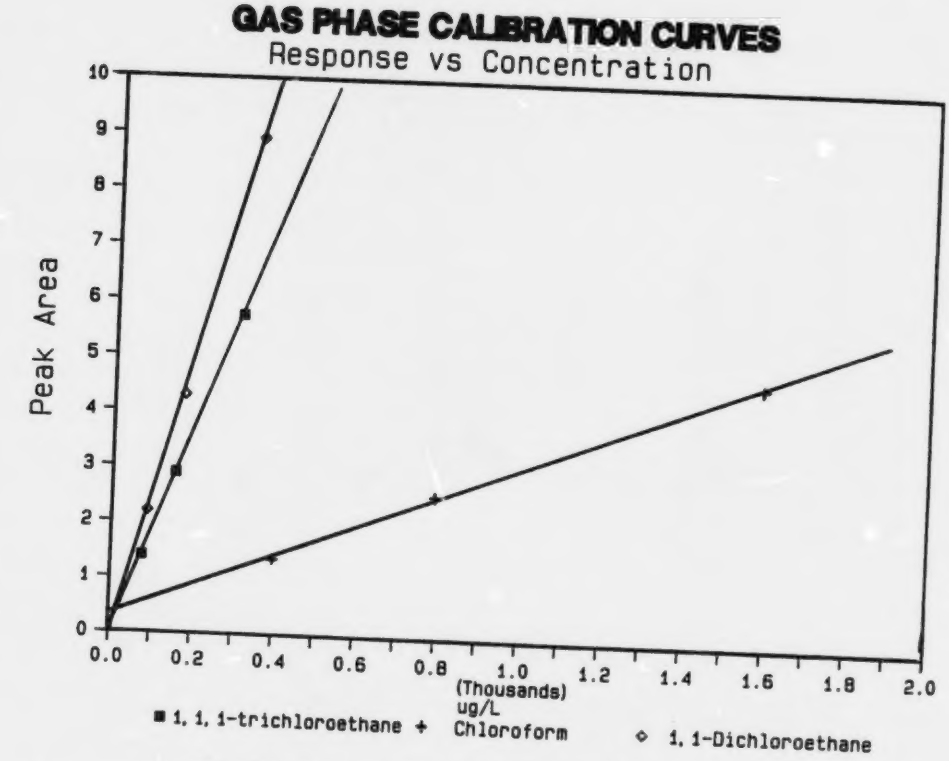

FIGURE 3B. THREE POINT CALIBRATION CURVES

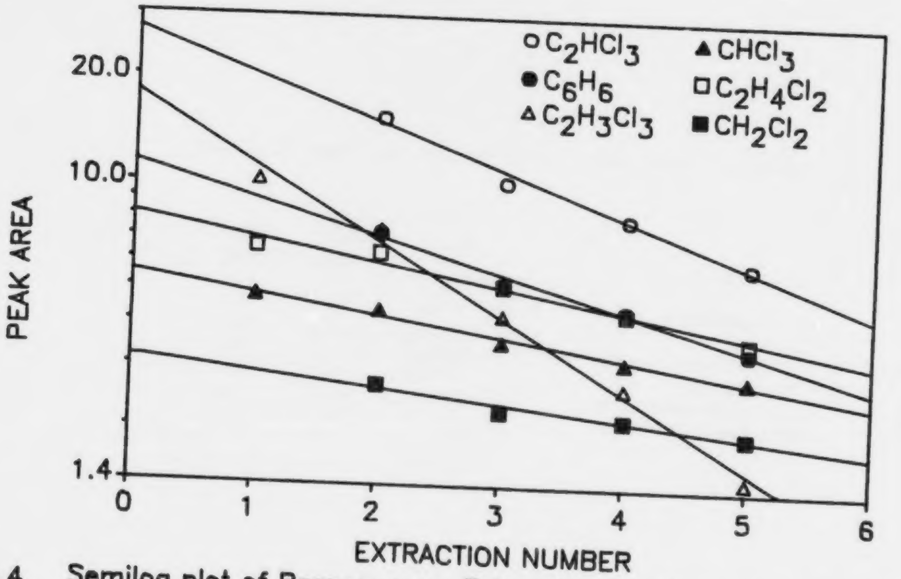

FIG.4 Semilog plot of Response vs. Extraction Number in Reagent Water

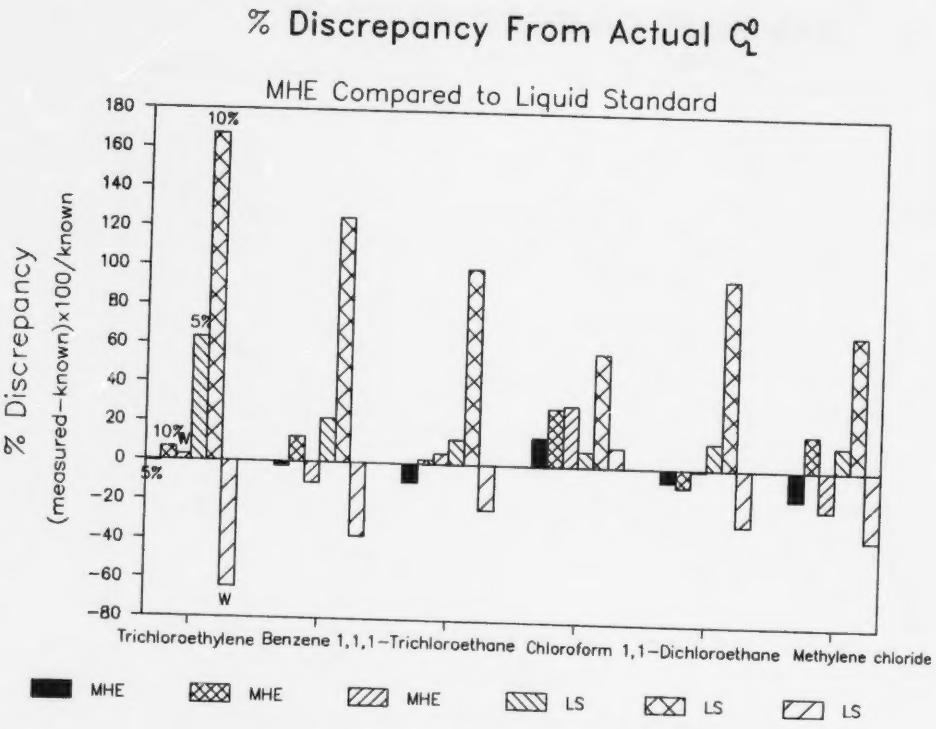

FIGURE 5. COMPARISON OF TWO DIFFERENT HEADSPACE METHODS

Table 1. Instrument Precision for Gas Phase Standards

Compound	Test Conc. ug/L	Avg. Peak Area	RSD % (n=5)
Trichloroethylene	16.4	10.6	8.2
Benzene	8	5.5	12.2
1,1,1-Trichloroethane	154.4	3.2	8.2
Chloroform	795.8	2.8	5.7
1,1-Dichloroethane	172.4	4.7	6.1
Methylene Chloride	49.1	2.6	4.4

Table 2. Results of Analysis of Six Volatile organics Using the Multiple Headspace Extraction Technique and the Liquid Standard Technique

5% NaCl Solution

		Multiple Headspace Extraction				Liquid Standard Technique			
	C ug/L Spike	C ug/L Found	RSD %	Discrepancy ug/L	Discrepancy %	C ug/L Found	RSD %	Discrepancy ug/L	Discrepancy %
Trichloroethylene	167.6	166.4	3.7	-1.2	-0.7	273.4	22.3	105.6	63.1
Benzene	80.9	79.3	10.3	-1.6	-2	98.8	10.5	17.9	22.2
1,1,1-Trichloroeth	1571.1	1423.9	4	-147.2	-9.4	1771.4	12.8	200.3	12.8
Chloroform	8094.5	9281.3	18.6	1186.8	14.7	8755.3	10.6	660.8	8.2
1,1-Dichloroethane	1753.5	1636.6	0.8	-116.9	-6.7	1992.6	8.1	239.1	13.6
Methylene Chloride	499.5	427.7	8.9	-71.8	-14.4	564.7	11.9	65.2	13.0

10 % NaCl Solution

		Multiple Headspace Extraction				Liquid Standard Technique			
		C ug/L Found	RSD %	Discrepancy ug/L	Discrepancy %	C ug/L Found	RSD %	Discrepancy ug/L	Discrepancy %
Trichloroethylene	167.6	178.5	0.5	10.9	6.5	448.0	20.5	280.4	167.3
Benzene	80.9	87.9	9.7	9.7	13	182.0	17.6	101.1	125.0
1,1,1-Trichloroeth	1571.1	1605.9	2.4	34.8	2.2	3146.1	12.5	1575.0	100.2
Chloroform	8094.5	10498.6	15.5	2404.1	29.7	12802.5	6.5	4708.0	58.2
1,1-Dichloroethane	1753.5	1591.2	3.7	-162.3	-9.2	3453.9	10.1	1700.4	97.0
Dichloromethane	499.5	590.7	2.7	91.2	18.3	847.0	6.0	347.5	69.6

Primary Waste Water Effluent

		Multiple Headspace Extraction				Liquid Standard Technique			
		C ug/L Found	RSD %	Discrepancy ug/L	Discrepancy %	C ug/L Found	RSD %	Discrepancy ug/L	Discrepancy %
Trichloroethylene	167.6	172.4	13.7	4.8	2.8	81.81	20.1	-85.79	-64.2
Benzene	80.9	74.3	10.6	-6.6	-10.6	50.11	9.3	-30.79	-37.6
1,1,1-Trichloroeth	1571.1	1659.2	8	88.1	5.6	1188	6.6	-383.1	-22.9
Chloroform	8094.5	10603.3	5.8	2508.8	31	7158	9.7	-936.5	10.1
1,1-Dichloroethane	1753.5	1744.4	18.4	-9.1	-0.5	1328	5.9	-425.5	-28.5
Dichloromethane	499.5	399.1	11.2	-100.4	-20.1	335.8	8	-163.7	-34.9

Table 3. Comparison of the Partition Coefficient (K) Found for each of the Six Volatiles in Reagent Water and Three Matrixes.

	K values			
	Reagent H2O	5% NaCl	10% NaCl	Waste Water
Trichloroethylene	2.9	1.9	1.0	3.2
Benzene	4.0	3.0	1.4	4.5
1,1,1-Trichloroethane	1.6	1.2	0.6	1.7
Chloroform	7.7	4.0	2.9	6.3
1,1-Dichloroethane	5.3	4.0	2.1	4.8
Methylene Chloride	11.1	7.1	6.3	7.1

DISCUSSION

JACK MURPHY: You say this saves time. If you do four or five extractions and run them on the GC, how long does it take to run one sample?

JAMES HO: You really don't need to take four or five extractions. If you get two or three good extractions, you can do it quickly. One extraction takes about ten minutes, and the analysis takes about ten minutes. Two or three good extractions would be enough.

BERNIE BERNARD: I found that two extractions are typically needed for the compounds that extract easily. What about something like tetrachloroethylene where might get into a situation where every extraction gives you basically the same amount?

JAMES HO: We haven't tried tetrachloroethylene. It probably would be a problem.

HAZARDOUS WASTE SITE MEASUREMENTS OF PPB LEVELS OF CHLORINATED HYDROCARBONS USING A PORTABLE GAS CHROMATOGRAPH

AMOS LINENBERG
PRESIDENT
SENTEX SENSING TECHNOLOGY, INC.
RIDGEFIELD, NJ USA

ABSTRACT

Portable Gas Chromatography has been established as an alternative to laboratory analysis, especially in hazardous waste site situations where analysis is required to be obtained at "Real Time".

For reliability and accuracy, however, the instrument to be used should include most of the features of a laboratory gas chromatograph, particularly, the ability to detect all compounds in question. This paper will describe the system used, the experiments conducted, and the results of various measurements of chemicals found in hazardous waste sites.

INTRODUCTION

The technique of Gas Chromatography offers considerable advantages when used for the detection of PPB levels of contaminants in air, water and soil. The features offered by this technique are as follows:

I. HIGH RESOLUTION.

II. HIGH SENSITIVITY.

III. DETECTABILITY OF A LARGE VARIETY OF COMPOUNDS.

IV. REPRODUCABILITY AND ACCURACY IN IDENTIFICATION AND QUANTIFICATION OF COMPOUNDS.

While those features are easily obtained in the laboratory, a field operating gas chromatograph must include all the necessary operational capabilities to obtain these features in an on-site analysis.

I. HIGH RESOLUTION.

Resolution is determined by the following parameters:

A. Ability to change columns.
B. Ability to use columns of different length.
C. Capability to use capillary columns or packed columns depending upon resolution needed.
D. Efficient injection system - a heated on column injection or efficient adsorption/desorption system.
E. Stable and evenly controlled column oven.
F. Temperature programming.
G. Low Volume detector cell to accommodate capillary columns.

II. HIGH SENSITIVITY.

High sensitivity is obtained by using the proper detector for the compounds to be detected. A Photoionization Detector, Argon Ionization Detector and Electron Capture Detector can be used. A Thermal Conductivity Detector does not have the sensitivity for low level measurement; a Flame Ionization Detector can be used, but it is cumbersome to operate in the field. In addition, a preconcentrator could be used to obtain ultra high sensitivity or to comply with certain federally-recommended methodologies.

III. DETECTABILITY OF VARIETY OF COMPOUNDS.

Certain detectors will allow the detection of different compounds. The Photoionization Detector can detect most organic compounds if a proper light source is used. The 11.8 E.V. light source will detect all organic compounds except those with a higher ionization potential. Since the lifetime of this light source is short; however, the light source which is used most frequently is the 10.6 E.V. source. Although this detector is sensitive to many organic compounds, it is quite insensitive to typical hazardous waste site compounds such as: Dichloroethane, Trichloroethane, Carbon Tetrachloride, Chloroform, Methylene Chloride and other compounds which have ionization potentials about 10.6 E.V.

The Argon Ionization Detector, with an energy of 11.6 E.V. will detect all the above compounds and is also, a rugged and reliable detector easily operated on site without a flammable gas source.

The Electron Capture Detector is extremely sensitive and relatively easy to operate but is selective only to commonly found volatile halogenated compounds.

IV. REPRODUCABILITY AND ACCURACY IN IDENTIFICATION OF COMPOUNDS.

The ability of the gas chromatograph to reliably identify compounds is a function of its ability to reproduce results. This ability requires stable temperature and flow conditions. More important, the calibration method used for the identification should be an accurate one which uses certified standards for each compound to be detected. The use of computerized methods, in which one calibrant is used to analyze a number of compounds is a relatively inaccurate method, and errors in both identification and quantitation of compounds may occur.

EXPERIMENTAL

The purpose of the experiment was to identify and quantify various chlorinated hydrocarbons of the type which are commonly present at hazardous waste sites. The main object was to separate and detect those hydrocarbons in the presence of various solvents such as Hexane, MEK, and gasoline vapors.

The compounds to be analyzed were:

Vinyl Chloride
1,1 Dichloroethane
1,2 Dichloroethane
1,1 Dichloroethene
1,2 Dichloroethene
111 Trichloroethane
112 Trichloroehtane
Trichloroethene
Methylene Dichloride
Tetrachloroethylene

The instrument used was the SCENTOGRAPH Portable Gas Chromatograph. Both capillary and packed columns were used for the separation. Temperature was varied from 40 deg. C to 110 deg. C. The detector employed was an Argon Ionization/Electron Capture Detector. The Argon Ionization Detector was suitable for the detection of all compounds. This detector, when operated as an Electron Capture Detector, detected the chlorinated compounds without interferences of other hydrocarbons. PPB level measurements were obtained by using the preconcentrator with the Argon Ionization Detector or by an injection of 1 cc of air sample to the gas chromatograph using the Electron Capture Detector.

Temperature programming was used to shorten analysis time. Because the SCENTOGRAPH is operated from a built in lap-top computer, all results and chromatograms were stored on disk for future reference. Calibrations were stored independently so as to allow access at future waste site evaluations, obviating the need for subsequent preparation of calibration standards.

RESULTS

Using different columns, complete resolution of all compounds was obtained. Please see Figure 1 and 2 for a typical chromatogram. The main difficulty appeared in the determination of vinyl chloride, for two reasons: Due to its high volatility, its retention time is relatively short and it was difficult to detect it using the same column used to separate the heavier compounds. In addition, the Electron Capture Detector did not respond well to the vinyl chloride and, therefore, it was more difficult to detect it from the other solvents.

Standards for calibration obtained from a specialty gas company were certified to the PPB levels. Other standards were prepared by mixing compounds in teflon bags.

CONCLUSION

Accurate on-site analysis of chlorinated hydrocarbons were carried out by using the SCENTOGRAPH. All results were recorded on the computer disks. Complete resolution of all compounds was obtained down to the concentrations in the PPB range. The Argon Ionization Detector coupled with a preconcentrator was used for general analysis; the Electron Capture Detector was used when interferences from other solvents were present.

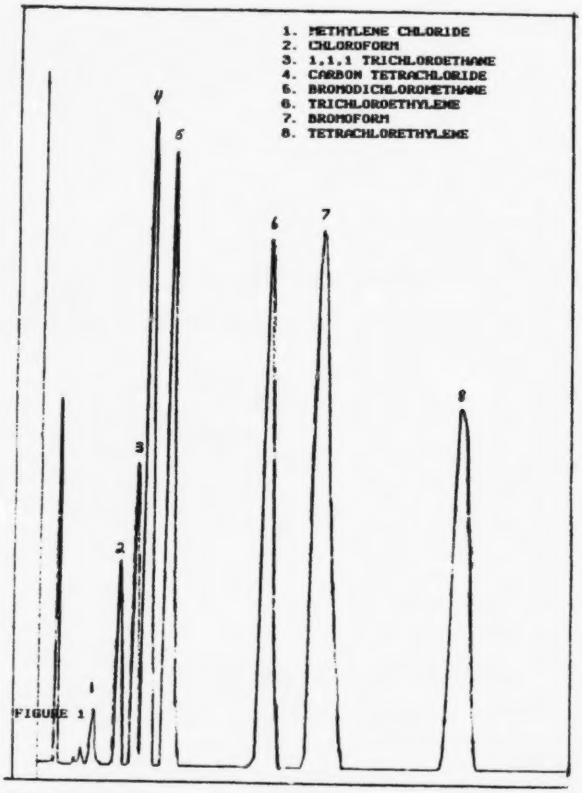

FIGURE 1

Column used: 10' long x 1/8" o.d. teflon packed with 20% SP2100/.1% Carbowax 1500 on 100/20 Supelcoport
Detector: Argon Ionization, Column Pressure: 22 PSI, Column Temperature: 50 deg. c,
Preconcentrator: Tenax, Sampling Time: 10 seconds, Concentration levels of all compounds tested were at 1 ppm + or - 10%

Column used: 6' aluminum 1/8" o.d packed with 20% SP2100/.1% Carbowax 1500 on 100/120 Supelcoport
Detector: Argon Ionization
Column Pressure: 20 PSI
Column Temperature: 75 deg. c.
Preconcentrator: Tenax
Sampling Time: 10 seconds
Concentration Levels of the four components tested were at:
Trichloroethylene: .5 ppm
1,1,1 Trichloroethane: 2 ppm
1,1,2 Trichloroethane: 2 ppm
Methylene Dichloride: 2 ppm

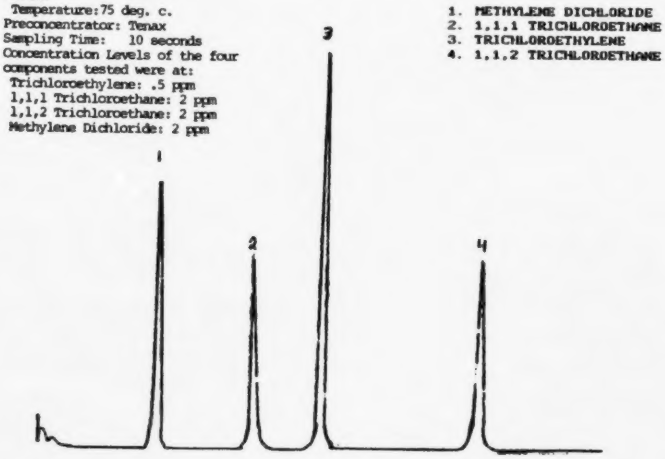

FIGURE 2

DISCUSSION

AVRAHAM TEITZ: Have you used any of the equipment for air sampling, and have you had any problems with it for ambient air sampling? I have known some organizations that have had some problems.

What kind of sensitivity can you get using the Sentex® for ambient air sampling?

AMOS LINENBERG: You can go to the ppb level.

AVRAHAM TEITZ: Is it possible to get to the sub ppb level, for say 1,1,1-TCA?

AMOS LINENBERG: It's not intended to go below the ppb level. In the field, I would safely say that we can see 5-10 ppb easily without pushing it too much. With chlorinated compounds, especially those that are responding to ECD, we can go below the ppb level.

CORRELATION CHROMATOGRAPHY WITH A PORTABLE MICROCHIP GAS CHROMATOGRAPH

Edward B. Overton, Robert W. Sherman,
Charles F. Steele and Hettihe P. Dharmasena
Institute for Environmental Studies
Louisiana State University, Baton Rouge, Louisiana 70803

ABSTRACT

The identification of unknown volatile organic compounds is of great interest for chemical hazard assessments. The speed in which these toxic chemicals can be identified and their concentrations determined is particularly crucial in emergency spill situations. A portable microchip gas chromatograph used with correlation chromatographic techniques allows for rapid on-scene identification of volatile organic compounds at part-per-million levels. The Gas Analyzer uses two temperature controlled capillary microchip gas chromatographs with different stationary phases for qualitative and quantitative analysis. It is interfaced with a Macintosh personal computer which uses special software to identify unknown compounds and integrates the peak areas in a chromatogram. Each sample is simultaneously analyzed on two different chromatographic columns having different stationary phases. The resulting retention times are compared to a library of normalized retention times for a variety of volatile organic compounds. Correlation chromatography is used to insure the positive identification of components in an unknown sample by requiring that the library-matched identifications for both gas chromatographic columns must be in agreement.

INTRODUCTION

Chemical hazard assessments at spill incidents and Superfund Sites commonly require the compound-specific qualitative and quantitative analyses of unknown volatile organic compounds. Further, these analyses should be rapid. Since traditional laboratory-based analyses are time consuming and expensive there is an urgent need for the development of rapid field-deployable analytical methods. A new compact microchip gas chromatograph (GC), containing two independent temperature controlled capillary column gas chromatographs, allows for rapid on-scene identification of volatile organic compounds at part-per-million (ppm) levels. Correlation chromatography techniques (1) have been adopted to aid in the identification of unknown compounds by comparing the retention indices obtained from the simultaneous analysis of samples on two GC columns coated with stationary phases of different polarity.

EXPERIMENTAL

The Microsensor Gas Analyzer (model 200, Microsensor Technology Inc., Fremont, California) is a small, portable instrument which uses two temperature controlled capillary microchip gas chromatographs with different stationary phases. The columns in the Gas Analyzer were coated with DB-1 or DB-5 and DB-1701 liquid phases by Microsensor Technology. Gas chromatographic run times on the microchip GC were on the order of one minute.

The Microsensor Gas Analyzer was interfaced with a Macintosh personal computer (Apple Computers, Cupertino, California) for acquisition and treatment of chromatographic data. The software allows for the display of chromatographic peaks, automatic peak detection and base-line assignment, area integration, and matches the sample peaks of a chromatogram with a normalized library of retention times or retention indices for unknown compounds run on each liquid phase.

Qualitative information was obtained for an unknown sample by use of a modified Kovats Retention Index System (2). The retention indices for compounds on columns of different polarities were compared. Positive identification of a given compound was made only if the retention index for both columns matches standard values (1) in a library accessed via the Macintosh computer. Table 1 gives a portion of the retention index libraries for selected volatile compounds of interest in environmental analyses.

A series of gaseous standards were injected via a pressurized sample loop onto each column and the retention times determined. From this, retention indices were calculated. This information served as a reference for the analyses of unknowns. Various components in a gaseous mixture were analyzed using correlation chromatography on the

Microsensor Gas Analyzer. A gaseous mixture was introduced into the Gas Analyzer and simultaneously analyzed on both chromatographic columns. Figure 1 shows an example of capillary GC analyses of a standard mixture on DB-5 and DB-1701 columns. The difference in retention times for various compounds is illustrated. Figure 2 shows retention indices calculated for a set of compounds on DB-1 and DB-1701 columns. These data were normalized using straight chain hydrocarbons (C_4 through C_{11}) standards, to provide retention indices that were used for compound identification.

SUMMARY AND CONCLUSIONS

High resolution can be best obtained by using capillary columns (1). Selectivity may be obtained by changing the temperature of the column or using two columns coated with stationary phases of different polarity. The Microsensor Gas Analyzer has all of the above features which lends itself to excellent qualitative and quantitative capabilities.

The size, two capillary columns, correlation chromatography and temperature control of the columns are features which make the Microsensor Gas Analyzer attractive for field use. The interface of the Gas Analyzer with the Macintosh allows for qualitative and quantitative information with a user-friendly system.

ACKNOWLEDGMENTS

The financial support for this work was provided by the National Oceanic and Atmospheric Administration, U.S. Department of Commerce, Contract No. 50-ABNC-7-00100.

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Table 1. A selection from the retention index libraries for DB-1 and DB-1701 columns.

GAS	DB-1701 2.5 meters 0.5 µ film	DB-1 1.75 meters 0.5 µ film
HEXANE	600	600
DICHLOROMETHANE	604	514
trans-1,2-DICHLOROETHYLENE	607	550
ISOPROPYL ALCOHOL	612	488
1,1-DICHLOROETHANE	640	557
ACRYLONITRILE	642	495
VINYL ACETATE	648	565
CYCLOHEXANE	669	660
ETHYL ACETATE	683	601
2,2,4-TRIMETHYL PENTANE	683	692
1,1,1-TRICHLOROETHANE	684	630
CARBON TETRACHLORIDE	685	650
TETRAHYDROFURAN	687	615
METHYL ETHYL KETONE	690	572
CHLOROFORM	695	597
HEPTANE	700	700
BENZENE	709	645
1,2-DICHLOROETHANE	727	621
TRICHLOROETHYLENE	740	683

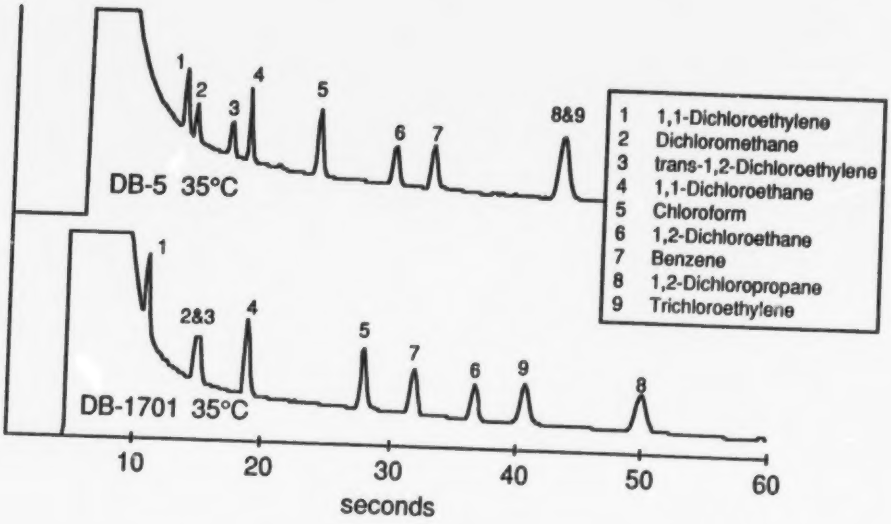

Figure 1. A gaseous mixture analyzed on DB-5 and DB-1701 columns of a Microsensor Gas Analyzer, model 200 (Microsensor Technology Inc., Fremont California).

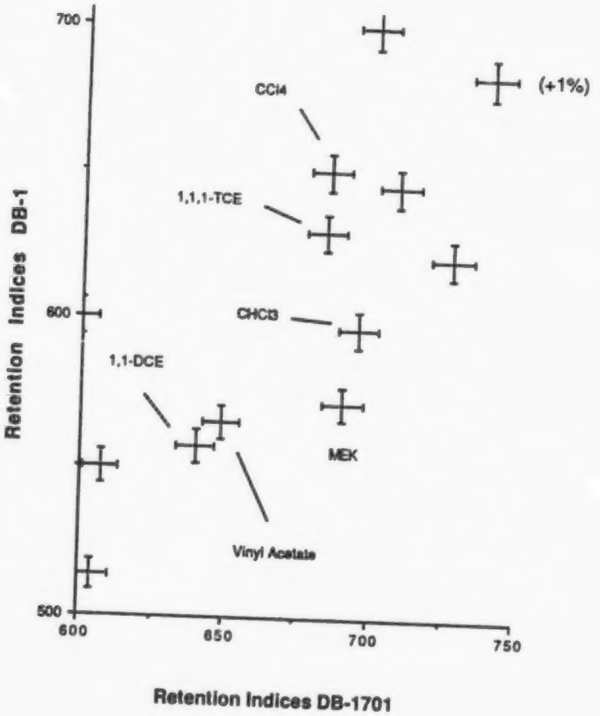

Figure 2. Retention indices calculated for a set of compounds on DB-1 and DB-1701 columns of a Microsensor Gas Analyzer, model 500 (Microsensor Technology, Inc., Fremont California).

DEVELOPMENT OF A FIELD PORTABLE CONCENTRATOR/PURGE AND TRAP DEVICE FOR ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR AND WATER SAMPLES

Robert W. Sherman, Edward S. Collard, Michael F. Solecki,
Tom H. McKinney, Linda H. Grande and Edward B. Overton
Institute for Environmental Studies
Louisiana State University
Baton Rouge, Louisiana 70803

ABSTRACT

Volatile organic compounds (VOC) are frequently found at very low concentrations in ambient air and water samples. To aid in the detection of these compounds, a portable device has been developed which concentrates VOC analytes from field samples on solid sorbent traps. The traps are made with a combination of Tenax GC and Spherocarb absorbants which allow efficient trapping of compounds with volatilities ranging from those of vinyl chloride to dichlorobenzene. Relatively small volumes (200-500 mL) of ambient air samples are concentrated by factors of 100 to 300. Additionally, this concentration device allows the purging of analytes from water samples and trapping the analytes on the solid absorbents. The concentrated samples may then be analyzed using appropriate field gas chromatographic instruments.

INTRODUCTION

The detection of volatile organic compounds in field samples at sub-part-per-million levels is difficult using current laboratory instrumentation and state-of-the-art field instrumentation. It is necessary that field samples be concentrated to a level which is above the instrument detection limits for these types of analyses. A portable concentrator/purge and trap device may be used in the laboratory or in the field to enhance the rapid detection of volatile pollutants or hazardous compounds.

Tenax GC and Spherocarb absorbants are both layered in an extremely small glass lined tube (11.4 cm with 0.7 mm i.d.) and used to trap volatile organic compounds of interest. These two absorbants retain compounds having a fairly wide range of volatilities. Tenax GC (1,2) and other sorbents (3) have been used to trap organic compounds in air. It has been determined that a Tenax GC-Spherocarb combination is well suited for field analyses of air and water (4). These combined absorbents trap compounds with a fairly wide range of ambient temperature vapor pressures (2-2500 mm Hg) and allow complete purging of the trapped compounds at elevated temperatures.

APPARATUS

A portable, metal case is used to house the concentration device, which is primarily composed of two solid sorbent traps (Figure 1). Each trap has its own heating unit, gas intake and outlet, and appropriate valves. Controllers and indicators are used to maintain a given temperature for a trap and provide appropriate flow rates of carrier gas through a trap. Since two traps are present in the concentrator, it is possible to accelerate the analysis time for a sample. While one trap is desorbing, the other trap can accept the next sample.

An air sample (200-500 mL) is injected onto a trap using an appropriate loading device such as a syringe, the trap is heated to 230°C, and helium is then used to flush the trap of any desorbed organic compounds. A concentrated sample is collected (this volume is adjustable) into another syringe and is ready to be used in any chromatographic instrument.

For water analysis, a cap fitted with two tubes is placed on a vial containing a 5 mL sample (Figure 2). One tube extends to the bottom of the vial and is used to introduce the helium purge gas. The other tube collects the purged gases from above the sample. The purged gases are fed directly into the load port of a Tenax GC-Spherocarb trap. A flow meter indicates the amount of gas which has passed onto the trap. From this point on, the VOC in the water sample are concentrated in the same manner as an air sample.

A battery of compounds has been tested for use with the concentrator. The percent recoveries for compounds with volatilities ranging from those of vinyl chloride to dichlorobenzene have been in the range of 40-70%.

FIELD USE

An air sample may be collected in the field and injected directly into the concentration device. A field sample may also be collected in a bag or some other approved container and returned to a laboratory for analysis via the concentrator and appropriate

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analytical instruments. Water samples may be purged and analytes trapped using the concentrator in the field or in a laboratory.

The concentrator has been used on several occasions for air monitoring and water analysis. Figure 3 shows an air sample that has been analyzed with and without the use of the concentrator. It can be seen that the concentrator enhances the analysis of any sample by raising the concentrations of volatile organic compounds above the limits of detection of a chromatographic instrument. Figure 4 shows an analysis of the headspace of a typical water sample, and the analysis of the same water sample after concentration by the purge and trap device. Again, low levels of compounds are detected in the concentrated sample which would not have been noted in the unconcentrated sample.

SUMMARY AND CONCLUSIONS

The use of the concentration device in conjunction with chromatographic instrumentation enhances the analyses of samples by allowing lower limits of detection for volatile organic compounds in air and water. Since the concentrator is the size of a small tool box, it is easily transported into the field to aid in analytical testing at various types of sites. The concentrator is flexible since the sample volume and concentrated volume are not fixed. The temperature of the traps may be varied to suit the needs of a given analysis. In addition, sample analyses may be obtained quickly since two traps are available. This concentration device is convenient for detecting levels of volatile organic compounds in air and water that have previously been impossible for a given chromatographic instrument.

ACKNOWLEDGEMENTS

The financial support for this work was provided by the National Oceanic and Atmospheric Administration, U.S. Department of Commerce, Contract No. 50-ABNC-7-00100.

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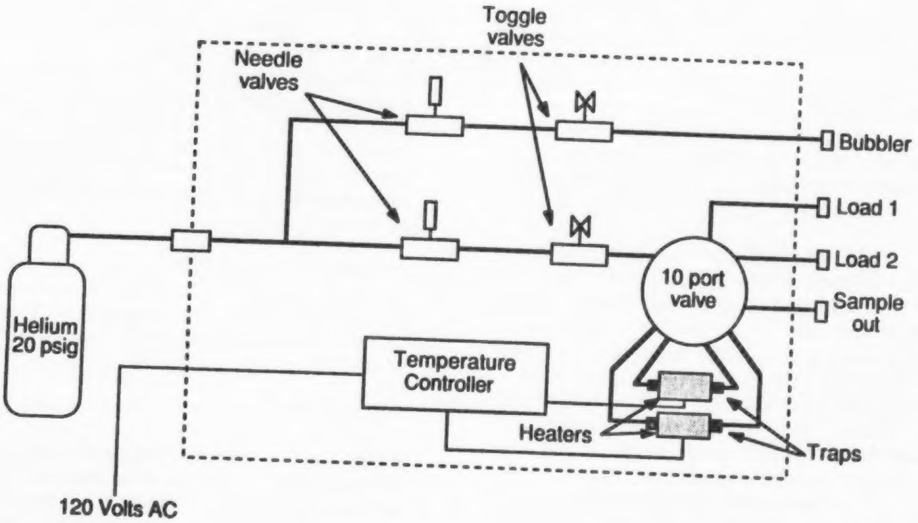

Figure 1. Schematic of concentrator/purge and trap device.

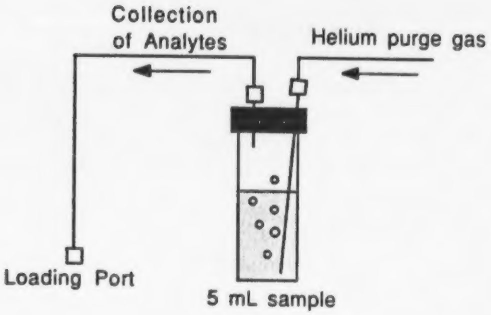
Collection
of Analytes
Helium purge gas
Loading Port
5 mL sample

Figure 2. Glass vial for purging and trapping water samples. Stainless steel needles and Teflon tubing are used for the introduction and collection of gases.

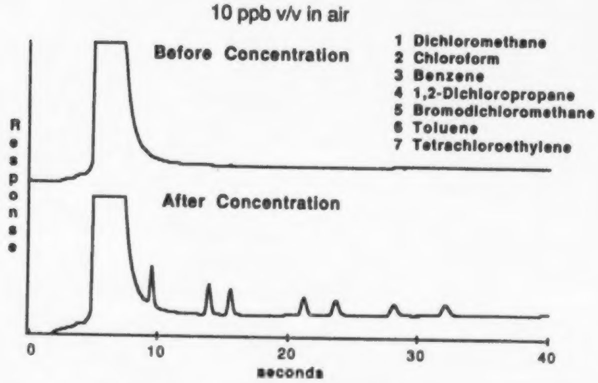

Figure 3. Analyses of a 10 ppb air sample with a Microsensor Gas Analyzer, Model 200 (Microsensor Technology, Inc., Fremont, CA), and the same sample concentrated 500 mL/1.5 mL using the concentrator device.

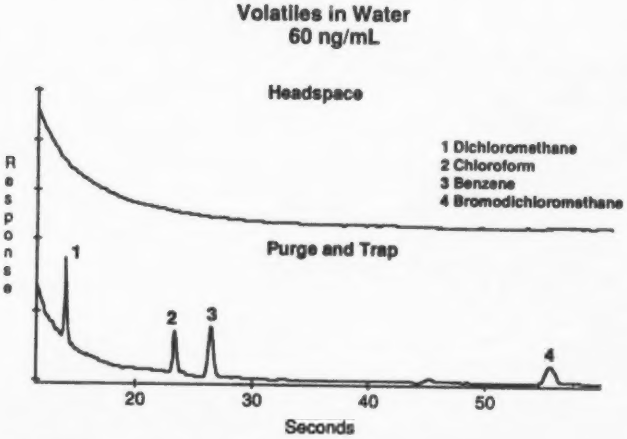

Figure 4. Analyses of the headspace of a water sample with a Microsensor Gas Analyzer, Model 200 (Microsensor Technology, Inc., Fremont, CA), and the same sample purged and trapped using the concentrator.

DISCUSSION

JOE SOROKA: What would you estimate is the upper limit for the concentrations for your purge-and-trap device? You're using only a very little amount of Tenax® (unless you break) therefore the volume is going to be very low.

ED OVERTON: The upper limit that we recommend is the detection limit of the analytical device, without concentrations. If we use the microchip GC, it can detect about a part per million, without concentration. You would screen the sample very quickly and see if you got anything. If you don't have anything, then you can run it through a concentrator to concentrate the organics.

JOE SOROKA: Is that screening by direct headspace?

ED OVERTON: That's the only way to do it. If you don't see anything by direct headspace, then you can do a purge and trap. Of course, you do the same thing for volatiles in air.

AVRAHAM TEITZ: When using the concentrator, what kind of detection limits do you have for organics? For air sampling using the concentrator, what are the detection limits?

ED OVERTON: It strictly depends on the detector that you use. If you use a photovac detector, the sensitivity will be lower. If you use a microchip GC, its detection limits are on the order of one part per million, and if you concentrate that by a factor of 300, you're down in the five to ten part per billion range.

The microchip GC that we use has a little bit lower detection limit, so you're on the order of one part per billion.

TOM SPITTLER: Do you have a rough idea of the cost of this instrument, and when it's likely to be on the market?

ED OVERTON: It is made and available right now from Microsensor Technology. It costs $8,000 for the GC. You have to use some software with it. I think they're selling a software package that requires the knowledge of a chemist (a timed-event software package).

Notice that the baseline was not flat, and so to get correct integrations, you have to use timed event, a tangent skim here, or a valley. We are working on a software package that has some intelligence built into it, that would integrate these peaks without having a chromatographer there. That is not quite available yet.

AL PLEVA: What do you use to plug the ends of your traps?

ED OVERTON: These things are permanently mounted, so they are plugged by the tubing that is connecting everything in there, so you always use the same trap. It's a basic difference between the commercially available trap device and this device.

AL PLEVA: What do you use to hold the Tenax® in?

ED OVERTON: A small piece of wire slightly bent. You load the trap, put the piece of wire in one end, and load in Spherocarb.® with a syringe. Then the Tenax® is loaded and wire forced in the other end.

AL PLEVA: Do you have any problem with water condensation on the wire.

ED OVERTON: We haven't seen any problems yet. I worry a little bit about our catalytic degradation, but so far, so good.

AL PLEVA: You're using Tenax® permanently mounted inside, is that correct?

ED OVERTON: That's correct. Tenax® and Spherocarb.® Tenax®, first plug, Spherocarb,® second plug.

AL PLEVA: Do you have any problems with memory or build-up over time, and how do you know when you've got to get rid of it, and replace it?

ED OVERTON: You've got to use exactly the same precautions you would use with any purge-and-trap device – that is at the high temperature, you purge your sample off, and then keep it at that temperature for another few minutes, drive off any contamination and then cool it back down.

What we do is typically run it up to temperature put a mL and a half through there, and then maybe run another 20 mL through before we lower it back down. If you use normal, good-quality analytical procedures, you won't have those problems. If, of course, you don't, you're going to have plenty.

AL PLEVA: How many uses do you estimate that you can get on the concentrator before you feel that you have to replace it?

ED OVERTON: We don't know yet. I would imagine several hundred cycles, but I don't know.

MICHAEL SOLECKI: I have several hundred runs on it, and I haven't had anything. And I always do couple of tests on it.

AL PLEVA: And what was the top temperature that you went to and when you went to desorption?

ED OVERTON: About 230, I think. We tried to come close to the standard technology, so we wouldn't have to reinvent any wheels.

DREW SAUTER: You mentioned not reinventing wheels. There is a piece of public domain software available that does background subtraction, and it's fairly sophisticated. It's actually written for mass spectroscopy, but you might want to look into that for background subtraction from chromatograms. I'll give you the listing.

ED OVERTON: This is not a trivial issue. We have run through more algorithms than I would like to count. When you try to do chromatographic integration without human intervention, you've got to go from highly tailed peaks to very broad peaks. We don't want to have to put, for instance, slope sensitivities in there. So we've got to have algorithms that take in all the things that a normal chemist does, without having a normal chemist there and that is a nontrivial task.

AMBIENT AIR SAMPLING WITH A PORTABLE GAS CHROMATOGRAPH

Richard E. Berkley
U. S. Environmental Protection Agency
Environmental Systems Monitoring Laboratory
Research Triangle Park, NC

ABSTRACT

The photoionization detector used in Photovac gas chromatographs is sensitive enough to detect certain kinds of hazardous compounds in milliliter samples of ambient air without preconcentration. Properly operated, such instruments can obtain data unspoiled by sampling errors and virtually free of negative interferences, so that upper limits to true concentrations can be estimated. Photovac portable gas chromatographs were originally designed for industrial hygiene analysis, typically at part per million analyte levels. At part per billion levels and below modification of the instrument and operating procedures was required. Rerouting carrier flow to continuously flush the sample loop and the flow control valves reduced carry-over contamination. Calibrant peak recognition criteria were changed so the correct calibrant peak would be recognized reliably. A constant-temperature oven stabilized retention times. Responses were enhanced by chromatographing a larger portion of the sample. Low-level calibration mixtures stored in SUMMA-polished cannisters reduced carry-over contamination by calibrant and permitted higher gain settings. Contamination was reduced by flowing calibrant and sample streams through the sample inlet for an extended period of time.

INTRODUCTION

Estimation of toxic organic vapors in ambient air is usually performed in a laboratory using samples which have been collected, transported, and queued pending analysis. An instrument capable of producing immediate results could avoid many errors which arise from these processes. Portable chromatographs, though less selective than laboratory instruments, can be even more sensitive and can rapidly produce data of known quality. Photovac portable chromatographs have a highly sensitive photoionization detector. The benzene detection limit has been shown to be less than one tenth part per billion (1,2). If operated properly they can be used for rapid screening of haloalkenes and substituted benzenes in air at typical ambient levels.

EXPERIMENTAL

Initial work was done with a Model 10S50 gas chromatograph which could automatically collect samples drawn through the sample inlet system by a small diaphragm pump. Late-eluting compounds were backflushed from a short precolumn after the intended analytes had entered the main column. Chromatographic operating parameters and solenoid valve timing were controlled through a keypad by an on-board microprocessor. Commercially available fused-silica wall coated open tubular columns (0.53 millimeter inside diameter) were used. They were hand-wound on a pasteboard spool just small enough to fit the ambient-temperature column enclosure. Carrier gas (ultrazero air) was supplied either from an internal tank or an external cylinder. Power was supplied by an internal battery which could be recharged when line power was available. An auxiliary external battery could also be connected. The width of the peak-recognition window could be set from the keypad and was a fixed number of seconds for all peaks in the chromatogram.

Calibration was done by analyzing known samples. The identity and concentration of each compound were entered into a calibration library in nonvolatile memory. Retention times of peaks on sample chromatograms were compared with those in the library. If they fell within a preset window the sample peak was "identified" as the corresponding compound and quantitated using the library response factor. Periodic recalibration was done by analyzing a single standard compound. Library concentration and retention time data for the standard were corrected, and concentrations and retention times for all other compounds in the library were corrected proportionally by the microprocessor.

After evaluation, the Model 10S50 chromatograph was upgraded to Model 10S70 and equipped with a constant temperature column enclosure. Columns specially encapsulated in epoxy resin must be used in the constant temperature oven. Column temperatures of 20, 30, 40, or 50 C can be set. The oven is powered by the external auxiliary battery. The width of peak-recognition windows is a percentage of retention time rather than a fixed number of seconds. The 10S70 is equipped with an internal modem so that it can be controlled by a remote computer. It can be operated locally either through the microprocessor keypad or through a microcomputer attached by RS-232 cable to the communications port. Software supplied by Photovac is used to control operating parameters and store data on disk.

In field sampling the instrument was operated either as a mobile or a stationary sampler. Mobile operation was done in an automobile using external auxiliary battery power and the internal carrier gas tank. The chromatograph was placed on the floor under the dash to shield it from direct sunlight, and a sample probe (1/8 inch stainless steel tube) was extended from the sample inlet through a window to about one meter above the roof of the car. All mobile sampling was done while the car was parked. Except during early morning or late evening, shaded locations were used. Stationary operation was done indoors using line power with an external carrier gas tank. The sample inlet was connected to a manifold into which exterior air was being drawn by a pump or fan, or the sample probe was extended outside the building from the pump inlet.

RESULTS AND DISCUSSION

Attempts to operate the 10S50 unattended at high gain were generally unsuccessful. The microprocessor identified the calibrant peak by elution order, and the wrong peak was usually chosen because many peaks were seen at high gain, the number of them being typically quite variable. Eventually it was discovered that increasing calibrant flow time from one second to ten seconds drastically reduced the number of extraneous peaks and made unattended operation possible, though it did not eliminate miscalibration entirely. Usually about half the data were spoiled. For this reason most work with the 10S50 was operator-attended mobile sampling. By contrast, the 10S70 requires the calibrant peak to meet both area and retention time criteria, and miscalibration has not occurred.

Preliminary field sampling in the vicinity of Research Triangle Park, NC using the 10S50 showed levels of benzene, toluene, and tetrachloroethylene near the bottom of the part per billion range or even lower. Results of sampling under field conditions were often spoiled by fluctuations in ambient temperature which caused peaks to miss retention time windows. This rarely happened to early-eluting compounds, since all windows had the same width regardless of retention time. If the window was set wide enough for late-eluting compounds to be seen, then it was much too wide to discriminate between early-eluting peaks. Often several early-eluting peaks were identified as the same compound because they all appeared in the same window. Frequent recalibration was of limited use in correcting library retention times. Such corrections functioned well for changes in flow rate and fairly well for slight changes in column temperature, but large temperature changes caused most compounds to elute outside their retention time windows.

A field trip to Houston, TX was made in March, 1987. The unit was equipped with a methylsilicone column operated in precolumn backflush mode. It was expected that fenceline monitoring in Houston would show substantially higher levels of benzene and toluene than could be found in Research Triangle Park, but levels of these compounds in Houston were really not much higher. Even close to obvious sources along the Ship Channel they were not much higher then levels reported at TAMS sites in nearby residential areas. A mixture of vinylidene chloride, trichloroethylene, and tetrachloroethylene in nitrogen, each at a concentration near 100 parts per billion, was used for field recalibration. Compounds which would have eluted later than tetrachloroethylene were backflushed. Significantly, the compounds most often seen were the very ones present in the recalibration standard. Typical data are shown in TABLE 1. It appeared that carry-over contamination of the sample inlet by calibrant might be occurring. Use of 100 parts per billion of calibrant constrained the gain setting to 100 or lower, which was not quite high enough to see ambient levels of most compounds. Furthermore, the microprocessor reported levels in units of parts per million only. Concentrations below 0.5 part per billion appeared as "0.000 parts per million". Such results, though not quite untruthful, are not quite useful.

In September, 1987 a field demonstration study was conducted in Richmond and Hopewell, Virginia. Personnel and equipment from EPA Region 3, Virginia Air Pollution Control Board Region 5, and EPA/EMSL, Research Triangle Park participated. During this study the 10S50 was operated as a mobile sampler from an automobile. It was equipped with a methylphenylsilicone column with 1.5 micrometer phase thickness which was operated without backflush. The flow system was modified so that carrier gas passed through the sample loop continuously except during sampling, and the entire volume of the sample loop was chromatographed. Some deterioration of peak symmetry and resolution resulted from this arrangement, but it was offset by enhanced sensitivity, enhanced baseline stability, and reduced carryover contamination by calibrant. In order to permit operation at higher gain and minimize calibrant contamination, a field recalibration standard of 10 parts per billion tetrachloroethylene was prepared by diluting a 100 part per billion commercial standard in a lecture bottle with ultrazero air. This mixture proved to be reasonably stable for several days. It was discarded and replaced after three days. Chlorobenzene, ethylbenzene, m-xylene, and o-xylene were added to the calibration library list. Standard concentrations were entered into the microprocessor at one thousand times their true values. This caused the microprocessor to report concentrations in the part per billion range as parts per million and eliminated the annoying problem of concentrations below 0.5 part per billion being reported as zero.

The 10S50 was operated at four sites in Richmond and nineteen sites in and around Hopewell. Some data early in the study were apparently spoiled by contamination of the inlet system from the interior of the car. The data in TABLE 2 show that responses to most compounds were highest in the first run at a site and trailed off to a minimum value during the next several runs. Increasing the sample pumping time from ten seconds to forty-five seconds eliminated this problem, as shown by the data in TABLE 3 which were taken near a large chemical plant in late evening. Apparently a large release of benzene and toluene occurred during the sampling period. Compounds eluting after tetrachloroethylene were not seen because ambient temperature was falling during the sampling period, and these compounds eluted outside their windows. Retention time stability was a serious problem throughout this study. Most sampling had to be done in early morning or late evening because daytime temperatures were much higher than the temperature at which the library had been created. Since optimum sampling conditions were transitory, many peaks were not recognized. It was clear that column temperature stability would have to be achieved before the instrument could attain full potential.

A study of air sampling methods was conducted during October, 1987 in Staten Island, New York. Personnel from EPA Region 2, the New York Department of Environmental Conservation, the State of New Jersey, and several local contractors participated. During this study the 10S50 was operated as a stationary sampler. It was located inside a school building. Outdoor air was drawn from a manifold. The site was about 3 kilometers downwind of the New York City Dump during the entire period of the study. It was also about 7 to 20 kilometers downwind of numerous chemical plants and oil refineries in New Jersey. Use of a ten second calibrant flow minimized extraneous peaks and permitted one all-night sampling period during which no data were spoiled by miscalibration. These data are shown in TABLE 4. Compounds eluting after chlorobenzene were not seen because of the retention time stability problem. The temperature in the room varied between about 70 - 80 F. About half the data were lost because of miscalibration during subsequent sampling.

After the Staten Island trip the 10S50 was upgraded to Model 10S70 and equipped with a constant temperature column oven. It was used in field sampling in Richmond and Hopewell, VA during June of 1988. The recalibration standard was a 14.6 part per billion dilution of chlorobenzene in a SUMMA-polished cannister. Most data were obtained while using the instrument as a stationary unattended monitor in a Virginia APCB station on Shirley Plantation. This site was 3 to 4 kilometers north of several chemical plants in Hopewell and about 1 kilometer east of two or three chemical plants at Bermuda Hundred. The wind was generally from the southwest to the west. Typical data are shown in TABLE 5. No miscalibrations occurred. Many more compounds per run were seen with the constant temperature column oven in use, especially late-eluting ones, but early eluting compounds such as benzene and trichloroethylene were seen rarely or not at all. Certainly benzene was actually present. Use of an earlier-eluting calibrant or a peak recognition window larger than + or - 2% of retention time may solve this problem. Retention time stability was much improved. The 10S70 reported data in parts per million or parts per billion, as appropriate.

Standard deviations of all retention time data obtained with the 10S50 during September, 1987 are compared in TABLE 6 with standard deviations of all retention times obtained with the 10S70 during June, 1988. Using the 10S70, column temperature fluctuated but carrier flow rates were not adjusted. Using the 10S70 column temperature was constant at 40 C, but flow rates were frequently adjusted in attempting to shorten the initial stabilization period. Nevertheless, standard deviations of retention times were nearly an order of magnitude lower.

CONCLUSIONS

The Photovac portable chromatograph, if properly used, can rapidly produce valid estimates of upper concentration limits of several classes of organic air pollutants. The optional constant-temperature column oven is practically a necessity for field use under most conditions. Further work should be done to determine the ambient temperature limits for operation of this unit and to fully assess the reliability of battery-powered operation with the constant temperature column oven under field conditions. Different types of columns should be tried so that other classes of compounds, especially polar compounds, can be analyzed.

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DISCLAIMER

The information contained in this article does not necessarily reflect Environmental Protection Agency policy.

Key words: Portable chromatographs, photoionization detectors, air analysis.

TABLE 1. SAMPLING AIR IN DEER PARK, TEXAS WITH PHOTOVAC 10S50

3-26-87 J. P. Bonnette Junior High School, 5010 West Pasadena Boulevard. Partly cloudy. Wind northeast light. 20 C. The Texas Air Control Board operated a TAMS site at this location.

Time	1,1-Dichloro-Ethylene	Benzene	Trichloro-Ethylene
	Parts per billion by volume		
1500	*	*	*
1513	2.0	<0.5	8
1524	*	*	*
1537	<0.5	<0.5	8
1549	ND	<0.5	5
1602	ND	<0.5	4

* Calibration run.

TABLE 2. SAMPLING AMBIENT AIR WITH PHOTOVAC 10S50 IN HOPEWELL, VA

9-15-87 403 Ramsey Avenue. In shade in front of house.
Wind light and variable. 30 C.

Time	Benzene	Tri-Chloro-Ethene	Toluene	Tetra-Chloro-Ethene	Chloro-Benzene	Ethyl-Benzene	m,p-Xylene	o-Xylene
	Parts per	billion	by volume.					
939				*				
959	6.64	1.38	7.58	1.58	ND	1.23	2.71	ND
1011				*				
1031	3.46	0.26	6.20	1.82	0.35	0.31	1.63	ND
1050	2.07	0.21	2.41	1.11	0.32	0.15	0.64	ND
1110	1.09	ND	1.39	1.07	0.36	0.13	0.37	ND

* This compound was calibrant in a calibration run.
ND Not detected.

TABLE 3. SAMPLING AMBIENT AIR WITH PHOTOVAC 10S50 IN RICHMOND, VA

9-24-87 South end of Commerce Street. About 500 meters downwind of a large
chemical plant. Wind very light W. 27-23 C.

Time	Benzene	Tri-Chloro-Ethylene	Toluene	Tetra-Chloro-Ethylene	Chloro-Benzene	Ethyl-Benzene	m,p-Xylene	o-Xylene
	Parts per	billion	by volume.					
1846				*				
1907	0.77	ND	2.46	0.36	0.26	ND	ND	ND
1926	0.87	ND	3.90	0.48	0.14	ND	ND	ND
1933				*				
1951	7.17	ND	12.46	0.19	0.12	ND	ND	ND
2013				*				
2033	64.14	6.24	47.44	ND	ND	ND	ND	ND
2049	72.49	7.10	46.98	ND	ND	ND	ND	ND

ND Not detected.
* This compound was calibrant in a calibration run.

TABLE 4. SAMPLING AMBIENT AIR IN STATEN ISLAND, NY WITH PHOTOVAC 10S50

10-21-87 Room 457, Susan Wagner High School, 50 Brielle Avenue, New York, NY. Sampler was connected to a manifold which was importing outdoor air.

Time	Benzene	Tri-Chloro-Ethylene	Toluene	Tetra-Chloro-Ethylene	Chloro-Benzene
	Parts per billion by volume				
0004	0.72	ND	14.6	0.07	ND
0019	0.72	ND	14.2	ND	ND
0034				*	
0049	0.70	ND	16.2	0.05	0.04
0104	0.70	ND	14.5	ND	0.07
0119				*	
0134	0.68	ND	15.8	0.19	ND
0149	0.75	ND	15.3	0.17	ND
0204				*	
0219	0.72	ND	15.8	0.30	ND
0234	0.80	ND	15.5	0.34	ND
0249				*	
0304	0.74	0.12	18.4	0.68	ND
0319	0.78	ND	20.0	0.21	ND
0334				*	
0349	0.91	ND	23.7	ND	ND
0404	1.16	ND	22.8	ND	ND
0419				*	
0434	1.47	ND	28.5	0.24	ND
0449	1.51	0.07	30.4	0.30	ND
0504				*	
0519	2.02	0.14	31.1	0.39	ND
0534	1.94	0.09	30.1	0.07	ND
0549				*	
0604	1.93	0.09	26.9	0.03	ND
0619	1.90	0.09	22.4	ND	ND
0634				*	
0649	1.85	ND	22.5	ND	ND
0704	2.12	ND	21.1	ND	ND
0719				*	
0734	2.11	0.08	20.9	ND	ND
0749	1.88	0.03	19.8	ND	ND
0804				*	
0819	3.22	ND	20.8	0.34	ND
0834	2.30	0.04	18.2	0.32	ND
0849				*	
0904	3.07	ND	19.2	0.39	ND
0919	3.65	ND	12.6	ND	ND
0934				*	
0949	2.95	0.10	21.1	0.27	ND
1004	3.29	0.13	21.3	0.29	ND

ND Not detected.

* This compound was calibrant in a calibration run.

TABLE 5. SAMPLING AT SHIRLEY PLANTATION WITH PHOTOVAC 10S70

6-22-88 Sampler was located inside Virginia APCB Station 75-B. Outdoor air was imported through the sample probe. Wind was 0 - 2 mph, SW to W. Station interior temperature was 78 - 75 F. Outside temperature was about 96 - 80 F. Plants at Bermuda Hundred were about 1.5 kilometer west-southwest. Plants at Hopewell were 3 - 4 kilometer south.

Time	Benzene	Tri-Chloro-Ethylene	Toluene	Tetra-Chloro-Ethylene	Chloro-Benzene	m,p-Xylene	o-Xylene	Styrene
	Parts per billion by volume							
1752					*			
1812	ND	ND	0.07	0.14	1.08	ND	ND	1.04
1832	ND	ND	0.10	0.16	0.79	ND	ND	1.19
1852	ND	ND	0.18	0.23	0.68	ND	1.74	0.89
1912					*			
1932	ND	ND	0.13	0.15	0.90	ND	23.1	ND
1952	ND	ND	0.25	0.21	0.70	ND	8.18	ND
2012	ND	ND	0.28	0.27	0.67	ND	2.94	ND
2032					*			
2052	ND	ND	0.26	0.24	0.75	ND	1.78	0.81
2112	ND	ND	ND	0.22	0.77	ND	24.0	ND
2132	ND	ND	ND	0.16	0.62	ND	22.5	ND

ND Not detected.
* Calibrant in a calibration run.

TABLE 6. COMPARISON OF RETENTION TIME STABILITIES USING AMBIENT-TEMPERATURE AND CONSTANT-TEMPERATURE COLUMN OVENS

	Toluene	Tetra-Chloro-Ethylene	Chloro-Benzene	o-Xylene
Ambient Temperature Column using 10S50 (September, 1987)				
Number of Samples	181	172	112	106
Maximum Retention Time	193.9	278.9	382.2	595.2
Minimum Retention Time (seconds)	108.5	153.3	211.8	325.3
Average Retention Time	139.1	201.4	280.7	424.9
Standard Deviation	16.4	26.1	34.4	52.9
Controlled Temperature Column in 10S70 (June, 1988)				
Number of Samples	81	47	85	54
Maximum Retention Time	229.2	257.0	459.2	609.5
Minimum Retention Time (seconds)	204.0	240.2	423.4	580.3
Average Retention Time	211.4	245.8	437.8	599.8
Standard Deviation	3.9	4.0	5.2	5.8

DISCUSSION

THOMAS SPITTLER: Looking at your data, I think they're extremely consistent with any kind of air pollution data that are reliable and have been published. We see a little benzene, toluene, occasionally a few chlorinated solvents in the air, and not much else. Within the last seven or eight years, since we've had the Photovacs® and done a lot of air studies, we still see almost exactly the same pattern.

It leads me to believe that we're not going to get a great deal of further information by doing air toxic studies widely and over a long period of time.

I think it's pointing us toward a lot more intensive study around specific point sources. A lot of data showed that as you were seeing some anomalies, you probably were looking at wind shifts blowing over specific sources, or specific plants.

That's the value of having this kind of instrumentation. When you're out in the field, when you see something, you can immediately move to it, you can track it and you can identify the sources. When you don't see some specific source, there is this very low background of a few parts per billion, something up in the range of five to twenty of benzene, toluene, and maybe a part per billion or less of chlorinated solvents.

RICHARD BERKLEY: I like being able to see the background when I'm out in the field. It reassures me a little bit that things haven't gone haywire. If I'm using an instrument that doesn't see anything below some fixed level above the background, then I have no way to be sure that the instrument is still working unless something suddenly shows up.

THOMAS SPITTLER: I found it particularly interesting that you had the canisters that you could take back and run through the desorption, the mass spectrometer, the chryofocusing and, and still see nothing significantly different.

RICHARD BERKLEY: I would like to do a lot more of that kind of work. I think more of it is called for to give us a greater volume of evidence. I would like to see more work done with different kinds of methods. If we had two or three methods agreeing with each other, it would be a tremendous burden of proof to anybody that questioned the results.

THOMAS SPITTLER: We were doing work at some of the very notorious waste sites up in New England, about five or six years ago. We came back occasionally from the study having found higher levels upwind than we found downwind of the site. When we had the time to go back and investigate, we'd find that the trichloroethylene we were seeing higher in the upwind was simply a matter of being closer to a dry cleaner in the neighborhood, some distance away from the site. The sites themselves showed very, very low levels of ambient toxics.

RICHARD BERKLEY: Yes, that is something that you can always run into in a crowded area – the possibility of some other site upwind.

Another thing I've encountered several times has been upwind diffusion, where the wind velocity was not uniform with altitude, and there would be still enough along the ground for diffusion. We would detect an extremely high level of something that should have been blowing away.

THOMAS SPITTLER: When you showed your slides of the house, I was curious as to whether you had taken the opportunity to take a sample inside and run it through GC. Did you do that?

RICHARD BERKLEY: No.

THOMAS SPITTLER: I came back from a hazardous waste site investigation, six or seven years ago, and had the Photovac with me overnight. I brought it into my house and took some samples in the bathroom, living room, and where we have our wood stove. I saw nothing within ten percent (10%) of the levels inside my house at the hazardous waste site we had investigated the entire day. We've been trying to find all these chemicals in the ambient air, where people spend very little time, and avoiding concentrating on interior environments, which are sometimes highly toxic, or at least have higher levels of chemicals in them.

We have diverted a lot of effort and attention into the ambient environment, failing to realize that we're living most of our lives in much more contaminated inside environments. That's beginning to come out now with some emphasis on indoor air monitoring. The portable gas chromatographs give us a tremendous handle on that, because they can go anyplace.

A PORTABLE SYSTEM UNDER DEVELOPMENT FOR THE DETECTION OF HAZARDOUS MATERIALS IN WATER

John C. Schmidt, Philip G. Koga, and Garland C. Misener
Environmental Technologies Group, Incorporated
Baltimore, Maryland

ABSTRACT

The development of an automated biosensor for use in the Monitor for Drinking Water Supplies (MDWS) is described. The biosensor is based on the inhibition of acetylcholinesterase covalently immobilized to a "clever" membrane and is projected to be sensitive to selected nerve agents and organophosphorus pesticides at the low ppb to low ppm levels. Projections for high reliability and low consummable cost are primarily due to the use of an improved fluidic scheme and "clever" membranes.

The technologies underlying two potential second generation chemical sensor modules for the MDWS are also discussed.

INTRODUCTION

A single instrument does not currently exist which is capable of rapidly detecting a wide variety of pathogens, biochemical toxins, and toxic chemicals in potable water pipes and water reservoirs. This paper will describe one part of the development of such a monitor for all three types of substances in drinking water samples.

The Monitor For Drinking Water Supplies (MDWS) is a modular instrument configured to sample drinking water from pressurized pipes, reservoirs and other water samples in the field. The system design is modular in order to facilitate the incorporation of new sensor technologies as they mature. The current design includes five modules: a chassis module, a sampling module and three sensor modules- one each for chemical, toxin, and biological threats. The modules are enclosed within a chassis and the entire system is controlled by a microprocessor.

This paper will describe the configuration and preliminary performance data of the first chemical sensor module, which is currently under development at Environmental Technologies Group (ETG), Inc. Other sensor technologies which may be incorporated into future chemical sensors will also be described. The first module detects very low levels of cholinesterase-inhibiting pesticides and nerve agents, and is based on the inhibition of acetylcholinesterase covalently immobilized to "clever" membranes. Since it is based on the effect of the analyte on the physiological target in the human body, this sensor is subsequently referred to as the biosensor. The use of "clever" membranes and enhanced fluidics are expected to result in producibility and selectivity improvements relative to previous enzyme-based systems. The other chemical sensor modules being considered for development are based on the electrochemical and ion mobility air monitoring systems developed at ETG, Inc.

DESCRIPTION OF THE BIOSENSOR CHEMICAL MODULE

The biosensor chemical module is the first sensor module being developed for the MDWS. It is designed to detect extremely low levels of nerve agents, organophosphorus pesticides, and carbamates. The biosensor module is based on the inhibition of the enzyme acetylcholinesterase, the physiological target of the nerve agents and these pesticides in the body [1,2]. As shown in Figure 1, the sensor consists of two syringe pumps, a sample loop, a membrane containing immobilized acetylcholinesterase, several Teflon valves, and a flow-through pH sensor. All of the fluid-wetted parts of the valves and lines are Teflon or Delrin in order to minimize adsorption of the analytes in the sensor.

The operation of the module can be divided into four phases and is summarized in Figures 1-2. In the first phase, the initialization phase, the buffered acetylcholine substrate solution is passed directly through the pH sensor and the pH of the solution is measured. This value is referred to as baseline 1. While baseline 1 is being determined, buffer is also passing through the membrane containing the immobilized enzyme (enzyme membrane) to establish equilibrium.

During the second phase, the uninhibited activity of the enzyme in the membrane disk is measured. The buffered substrate solution is routed through the enzyme membrane and then to the pH sensor. Since the enzyme hydrolyzes acetylcholine to choline and acetic acid, the activity of the enzyme membrane can be calculated from the pH change of the substrate solution before and after exposure to the the enzyme membrane. The initial, uninhibited, enzyme activity is actually the pH value measured during the second phase minus the baseline 1 value measured in the first phase.

Two tasks are accomplished during the third phase. First, the baseline is updated and, second, the enzyme membrane is exposed to the sample. The buffered substrate solution is once again passed directly through the pH sensor to update the baseline. This value is referred to as baseline 2. The measurement of the baseline during each odd cycle allows one to compensate for both long-term drift of the pH electrode and slow nonenzymatic hydrolysis of the substrate. Simultaneously, the sample injection valve is rotated such that the contents of the sample loop are routed through the enzyme membrane. Since the analytes of interest inhibit the enzyme, their presence in the sample can be determined in the next phase when the final "exposed" or inhibited enzyme activity is measured.

The inhibited enzyme activity is measured during the fourth phase. As in phase 2, this is accomplished by routing the buffered substrate solution through the enzyme membrane and then through the pH sensor. The inhibited enzyme activity is the value measured in phase 4 minus the baseline 2 value. The percent inhibition is calculated as follows:

Percent inhibition = 100 $(1 - A_i/A_u)$ where

A_i = inhibited enzyme activity
A_u = uninhibited enzyme activity

Since the percent inhibition of the enzyme is a function of the analyte concentration, a semiquantitative estimate of the analyte concentration can be determined by the algorithm in the instrument chassis.

In the absence of significant inhibition of the enzyme, phases 3-4 are repeated every six minutes. In the event that the enzyme activity drops below a preset level (either due to an exposure to analyte or a slow natural activity loss over several days), a new enzyme membrane is automatically moved into place. The process begins with phase one every time a new enzyme disk is initially used.

Two aspects of the four-phase cycle are worth noting. First, the selectivity of the module is enhanced by the fluid path during the third phase of the cycle. Most previous sensors of this type routed a mixture of the sample and substrate solution through the enzyme and pH (or voltammetric) module in a single step. Therefore, they were vulnerable to false alarms due to acid-base or redox interferents in the sample. Since the MDWS system described in this paper uses a two step process in which the pH sensor is never exposed to the sample, the selectivity of the MDWS sensor is enhanced considerably. Second, the sample turnaround or cycle time of the system is approximately 15 minutes. The cycle time is the sum of the sample acquisition and pretreatment time (in the sampling module), the sensor response time, and the algorithm response times.

Description of the Enzyme Membrane

The projected high producibility and low production cost of the biosensor module are primarily the result of the use of "clever" membranes to immobilize the acetylcholinesterase. The term "clever" membrane refers to a relatively new type of microporous membrane in which the surface contains a large number of aldehyde groups [3]. The aldehyde groups on the surface of the membranes form covalent bonds (Schiff bases) with amine groups on proteins. One very attractive feature of "clever" membranes is that many proteins can be immobilized by simply submerging the membranes in an aqueous solution of the protein. This eliminates the need for several relatively complex and time-consuming steps normally required during alternate covalent immobilization schemes. Significant improvements in reliability and decrease in consumable production cost are projected.

The biosensor module is loaded with several acetylcholinesterase membrane disks which are stored dry [4] and incorporated into a carousel. The device is configured such that a fresh enzyme disk can be rotated into place immediately after any assay in which the previous disk is depleted. The membrane material is microporous polyvinylalcohol approximately 5 mils thick [5]. Each enzyme disk is approximately 2 cm in diameter and contains approximately 3 units of acetylcholinesterase.

Description of the Substrate

Acetylcholine chloride is used as the substrate during the assay of the uninhibited and inhibited activity of the enzyme disk. The assay solution consists of 50 millimolar acetylcholine chloride in 3 millimolar phosphate buffered saline (PBS).

Preliminary Performance of the Biosensor Chemical Module

The preliminary sensitivity data for the chemical biosensor module is summarized in Table I. Figure 3 depicts the results of sampling deionized water containing 7.0 ppb VX (O-ethyl S-(2-diisopropylaminoethyl) methylthiophosphonate), an organophosphorus nerve agent. The acetylcholinesterase activity was inhibited approximately 28%. Since the percent inhibition of the enzyme is a function of the analyte concentration, a microprocessor-based algorithm can be trained to indicate a semiquantitative (high, medium, low) concentration of the analyte.

Table I. Preliminary Sensitivity Data For Agent VX

Percent Enzyme Inhibition	Instrument Display	Approximate VX Concentration
10-35%	low	5-10 ppb
35-75%	medium	11-99 ppb
75-100%	high	100+ ppb

The sensitivity of the biosensor chemical module will also be tested to the other nerve agents and pesticides listed in Table II. In general, the sensitivities are expected to be a function of the toxicity of the compound; the more toxic the material, the lower the detection limit of the sensor. The minimum detectable level of most of the cholinesterase-inhibiting analytes will probably range from low ppb to low ppm levels.

Table II. Pesticides and Other Nerve Agents To Be Tested on the MDWS

Analyte
Agent GD
Malathion
Parathion
Paraoxon
Neostigmine
Physostigmine

The selectivity tests planned for the chemical sensor are listed in Table III. The percent inhibition of the enzyme due to the interferent dissolved in deionized water will be measured to quantitate any false positive responses of the sensor. False negative responses will be measured by comparing the enzyme inhibition of 7 ppb VX to that of a solution of 7 ppb VX and the interferent.

Data collected to date indicates the sensor is capable of one week of continuous unattended operation. Typical enzyme disks maintain over half of their activity after one week of continuous operation. The substrate solution is also stable for one week under normal conditions. Both the reconstituted substrate solution and enzyme disk carousel must be replaced on a weekly interval during continuous operation. Both are stored dry, and have a shelf life of approximately 2 years at 25°C.

DEVELOPMENT OF FUTURE CHEMICAL SENSOR MODULES

The development of additional chemical sensor modules is also under consideration at ETG, Inc. Future chemical sensor modules will likely be based on modifications to current ETG air contaminant sensors. While these sensors were not selected for the initial chemical sensor because they are not ideal for the detection of the nerve agents of primary interest to the MDWS, they are capable of detecting the diverse list of chemical substances summarized in Table IV.

The sensor systems based on ion mobility spectroscopy are described in other papers presented during this symposium [6,7]. The electrochemical sensors produced at ETG, Inc are amperometric sensors; an exploded view of a typical amperometric sensor can be found in Figure 4. A typical amperometric sensor consists of three electrodes in contact with an electrolyte-saturated insulator. One of the electrodes, the sensing electrode, is separated from the sample by a microporous Teflon membrane. The pores of the membrane are small enough to prevent the liquid electrolyte from escaping, but large enough to permit ordinary diffusion of the analyte from the environment to the electrolyte. A permselective membrane on the ambient side of the microporous membrane provides an additional degree of specificity. The sensing electrode is biased at a potential sufficient to oxidize or reduce the analyte of interest. Electroactive compounds undergo redox reactions directly on the sensing electrode surface, resulting in a current which is proportional to the analyte concentration. Nonelectroactive compounds, such as the organophosphorous esters, are converted to electroactive compounds by a reagent in the electrolyte. Modulation of the sensing electrode potential by several differential or pulsed techniques has resulted in significant improvements in the sensitivity and specificity of this type of sensor in the past few years. Typical modulated sensors are capable of detecting as low as parts per billion (ppb) levels of many organic and inorganic air pollutants.

Amperometric gas sensors are now in widespread use in ambient air monitoring due to several inherent advantages of the technology. First, the sensors are inexpensive. All of the components shown in Figure 4 can be injection molded from inexpensive materials, stamped from inexpensive sheet stock, or otherwise processed using very small amounts of precious metals. Second, they are simple and reliable. There are no moving parts to fail, and the sensor output is usually a linear function of concentration. Third, they are portable. A self-contained system containing a sensor, associated electronics, battery, and readout device can easily fit into a shirt pocket.

The same advantages make amperometric sensors attractive candidates for several water monitoring applications. The cost, reliability, and size advantages of electrochemical air sensors are also important for water contaminant sensor applications. The configuration shown in Figure 4 has two additional advantages for water monitoring applications. First, the microporous membrane adjacent to the sensing electrode provides an air gap which separates the water sample from the electrolyte. This permits analytes with relatively high vapor pressures to enter the electrolyte and be detected. However, large molecular weight materials such as proteins which typically foul the electrodes of conventional electrochemical cells are prevented from entering the amperometric sensor. Second, a complicated sampling subsystem is not necessary to separate the analyte from the water sample as is the case with ionization and many other sensor systems, since water is a major component of the electrolyte of the electrochemical sensor. In fact, the aqueous sample simply flows past the microporous membrane in the simplest scheme under consideration.

Amperometric systems sensitive to cyanide, organic arsenicals, and organic sulfides have received the most attention to date. Decisions regarding the development of specific electrochemical sensor modules are expected to be made after the initial prototype MDWS system is tested in September 1989.

CONCLUSION

The preliminary performance testing of the MDWS chemical sensor module suggests that "clever" membranes can be used to improve the producibility and reduce the production cost of analytical systems based on immobilized enzymes. The minimum detectable level of the MDWS chemical module was approximately 5 ppb for the most toxic oganophosphorus cholinesterase inhibitor. A modification in the standard flow scheme improved the selectivity of the MDWS relative to most previous sensors based on the cholinesterase inhibition scheme.

When interfaced with the sampling module and chassis module in the MDWS system, the chemical sensor module will provide an automatic instrument capable of continuously monitoring low levels of cholinesterase inhibitors for one week periods without service. Several of the many potential applications for the MDWS include drinking water analysis, food analysis, and screening of Superfund sites.

Extensive expertise developed at ETG and Allied-Signal Corporate Laboratories in the development of trace level air monitors is currently being applied to develop MDWS sensor modules for biochemical toxins and pathogens. When the other sensor modules are completed, the MDWS will be the first automatic system capable of monitoring toxic chemicals, biochemical toxins, and pathogens simultaneously.

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3. Clever membranes are commercially available from three vendors at the time this article was written: MEMREE membranes from Micro Membranes, Inc. in Newark, NJ; Immobilon membranes from Millipore Corporation in Bedford, MA; and Ultrabind membranes from Gelman Sciences Inc. in Ann Arbor, MI.

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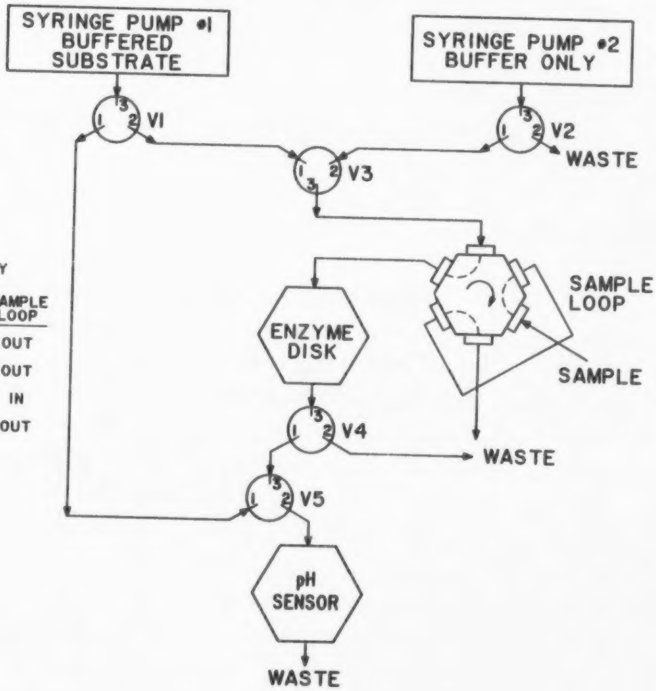
SYRINGE PUMP #1
BUFFERED
SUBSTRATE
SYRINGE PUMP #2
BUFFER ONLY
V1
V2
WASTE
V3
SAMPLE
LOOP
ENZYME
DISK
SAMPLE
V4
WASTE
V5
pH
SENSOR
WASTE

OPERATIONAL SUMMARY

PHASE	FLUID PATH V1	V2	V3	V4	V5	SAMPLE LOOP
1	31	31	23	32	12	OUT
2	32	32	13	31	32	OUT
3	31	31	23	32	12	IN
4	32	32	13	31	32	OUT

Figure 1. Schematic of the Biosensor

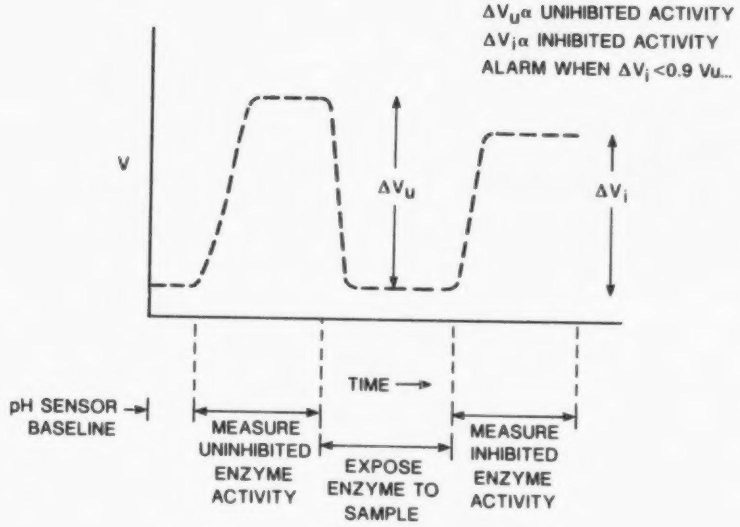
ΔVuα UNIHIBITED ACTIVITY
ΔViα INHIBITED ACTIVITY
ALARM WHEN ΔVi <0.9 Vu..
V
ΔVu
ΔVi
TIME →
pH SENSOR BASELINE
MEASURE UNINHIBITED ENZYME ACTIVITY
EXPOSE ENZYME TO SAMPLE
MEASURE INHIBITED ENZYME ACTIVITY

Figure 2. Idealized Response of the Biosensor

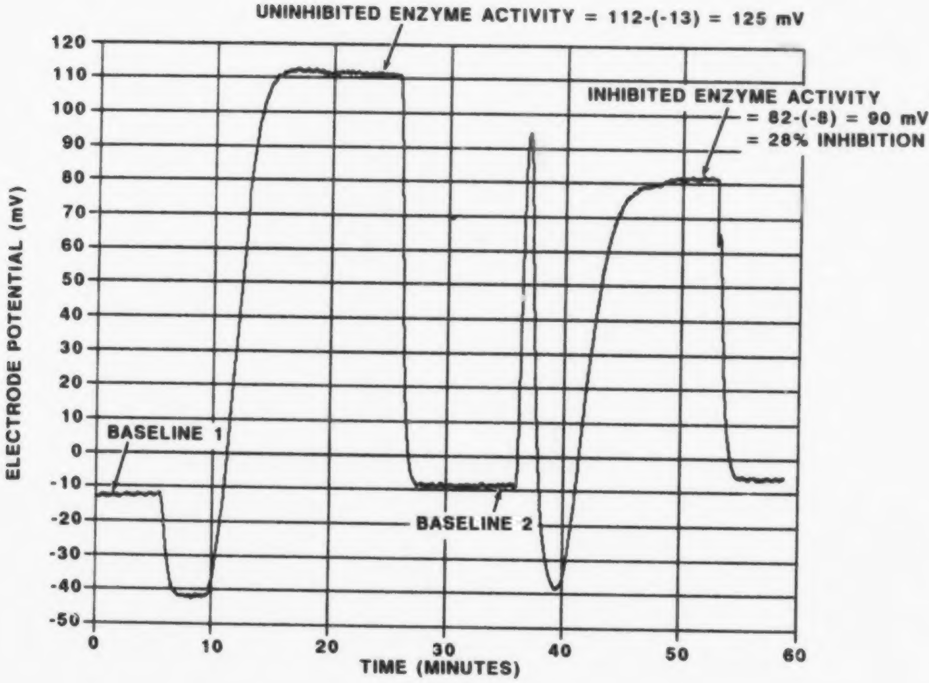

Figure 3. Response to 7 ppb VX

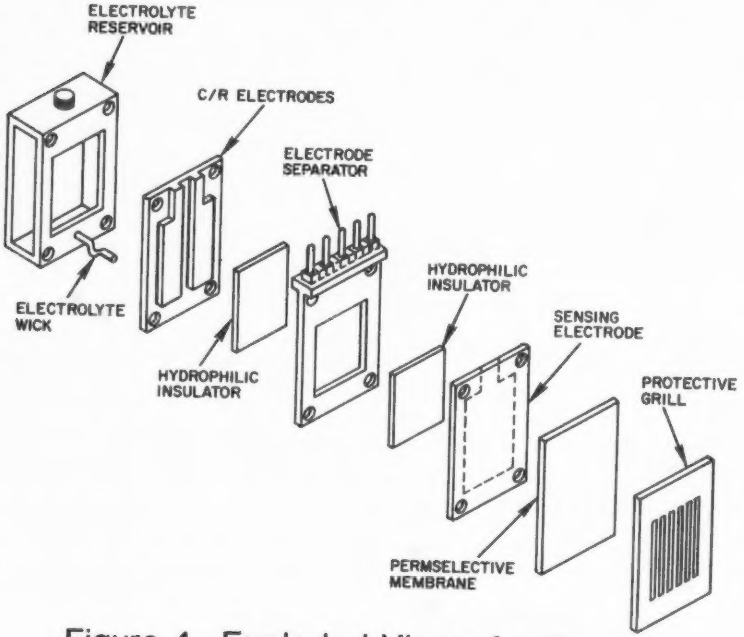
ELECTROLYTE RESERVOIR
C/R ELECTRODES
ELECTRODE SEPARATOR
ELECTROLYTE WICK
HYDROPHILIC INSULATOR
HYDROPHILIC INSULATOR
SENSING ELECTRODE
PROTECTIVE GRILL
PERMSELECTIVE MEMBRANE

Figure 4. Exploded View of a Typical Amperometric Sensor

Table III. Summary of Interferent Test Plan

Interferent	Concentration Tested	Interferent Tested For False Negatives	Interferent Tested For False Positives
Isopropanol	1,000 ppm	–	*
Unleaded gasoline	500 ppm	–	*
Trichloroethylene	500 ppm	–	*
Benzene	500 ppm	–	*
Chlorine	1 ppm	–	*
Zinc chloride	1,000 ppm	–	*
High [Mg+]	2,400 ppm	*	–
High [Ca+]	4,000 ppm	*	–
Tween 20	1 pct	*	–

* tests planned for late 1988

Table IV. List of Potential Chemical Sensors Under Consideration

Sensor Technology	Current EAS Product Name	Analytes Detectable in Air	
		Analyte	Detection Limit
Ion Mobility Spectroscopy	Advanced Chemical Agent Detector/ Alarm (ACADA)	Organophosphorus Esters	mid ppt
		Organic sulfides and arsenicals	low ppm
		Selected explosives	low ppb
		Many other organic compounds	ppt-ppm
	Chemical Agent Monitor (CAM)	Same as ACADA	
	Bendix IMS	Same as ACADA	
Electrochemistry	Individual Chemical Agent Detector (ICAD)	Organophosphorus esters	mid ppb
		Organic sulfides and arsenicals	low ppm
	Mini Alert	Hydrazines	mid ppb
		Many other electroactive gases and vapors	ppm-percent

DISCUSSION

ED HEITHMAR: Why did you choose the syringe pumps for your FIA system, instead of, say, a PD pump or something like that?

TAD BACON: That's a good question. It's still in the experimental stage, and what I've described here is just the first stage of development for this instrument. There is going to be a lot of miniaturization and expanding on this technique to use the most appropriate methods.

ED HEITHMAR: There is no pressure sensitivity for your detector?

TAD BACON: No.

ED HEITHMAR: I assume that the enzyme regenerates itself after a period of time, right?

TAD BACON: Actually, as long as it's not inhibited, and it's bound to the membrane, then it will retain its activity for a number of days. In this particular configuration, it will retain satisfactory activity for about three days. Not shown in the schematic is a network of microprocessors and controllers, which look at the information derived from the sensor. One of the things that they look at is the response of the sensor at the baseline level, where the enzyme is not inhibited, but when it's exposed to the acetylcholinide.

If that activity level falls below a certain point, a carousel will rotate a fresh disk into place, with original activity. In this way, you can run the system for about seven days. There would have to be about three or four disks.

ED HEITHMAR: Once it's been exposed to an agent, it's no longer usable.

TAD BACON: That's the other case. If inhibition occurs, the system would signal an alert to shut down the water supply, or whatever system is being monitored, and a new disk would be rotated in place.

DESIGN AND PERFORMANCE OF A MOBILE MASS SPECTROMETER DEVELOPED FOR ENVIRONMENTAL FIELD INVESTIGATIONS

Thomas M. Trainor, Ph. D. and Frank H. Laukien, Ph. D.
Bruker Instruments, Inc.
Manning Park
Billerica, Massachusetts 01821

ABSTRACT

Design goals set for a field mass spectrometer must address several conflicting demands, including instrument size, weight, power requirements, and capabilities. Based on a quadrupole analyzer and an electron-impact ionization source, the Bruker MEM is a complete GC-MS designed specifically for field operation and deployment in a 4-wheel drive vehicle. Power requirements are limited to 600 W, which is normally supplied by rechargeable 24 V batteries. Mass spectrometric capabilities include both full scan and selected ion monitoring (SIM) data acquisition modes. A variety of sampling accessories have been produced for the MEM, including a unique direct air/surface sampler, enabling direct analysis in under 15 seconds of water, soil, or air samples. In addition, a capillary GC equipped with a thermal desorption oven is available, permitting analysis of more complex mixtures. Applications to be discussed will focus on actual performance of the MEM in carrying out field screening of regulated volatile and semi-volatile organics, and will serve to critically evaluate the instrument's analytical capabilities.

INTRODUCTION

The enormous demands currently placed on organizations carrying out hazardous waste site assessments and remedial action activities have led many participants to consider direct field monitoring to augment or replace their dependence on traditional sampling/off-site analysis protocols. This concept of real-time, on-site analysis for environmental pollutants is becoming an increasingly attractive alternative to the data turnaround, sample degradation, and field mobilization cost problems often encountered in relying completely on off-site laboratory analysis. Standard organics analytical methods developed over the last decade by the US EPA for regulatory purposes under the major environmental programs (CERCLA, SARA, RCRA, NPDES, etc.) all embrace gas chromatography-mass spectrometry (GC-MS) as the preferred approach, due primarily to its demonstrated sensitivity and specificity (1,2). However, the bulk of the field analytical work conducted currently by the US EPA and private contractors is based on non-specific GC detectors (PID, ECD, FID, TCD, etc.) (3,4). Some attempts have been made in terms of field deployment of GC-MS instruments, originally designed for laboratory use, on-site in climate-controlled, stationary trailers which are often referred to as "mobile laboratories" (5). For a variety of reasons, this latter approach of introducing full-laboratory capabilities in the harsh field environment is often fraught with problems and is, with today's excellent network of overnight delivery services, of arguable benefit compared to off-site analysis at full service laboratories.

The development of a truly mobile mass spectrometer, that is, an instrument capable of reliable operation under a wide range of temperatures without auxiliary cooling, compressed gases, or ac power, now permits realistic field GC-MS activities. The Bruker Mobile Environmental Monitor (MEM) was developed from scratch with the following four major design goals in mind:

1. Resistance to extreme environmental operational conditions, e. g. extremes in terms of temperature, humidity, and mechanical/electrical shock.
2. Simple, easy instrument operation and sample preparation by individuals with a minimum of GC-MS training and experience.
3. Produce unambiguous qualitative and quantitative analytical results.
4. Provide constant monitoring of instrument performance with appropriate error messages reported automatically.

These design goals had to be met while simultaneously addressing several conflicting demands, including instrument size, weight, power requirements, and analytical capabilities. The final commercial civilian mobile mass spectrometer, the MEM, has evolved from a related product, the MM-1, developed earlier for the military market. The MM-1 is now a key chemical sensor of the West German Army for its land based reconnaissance vehicles and is currently undergoing extensive evaluation by the US military. The MM-1 is deployed to detect, identify, and quantify all chemical warfare agents in air or on surfaces, in real-time under battlefield conditions.

The purpose of this presentation is to evaluate in detail the unique hardware and software features incorporated into the MEM that permit routine trace level GC-MS analysis in the field. Results in terms of instrument sensitivity, linearity, accuracy, reproducibility, and stability will be presented in the context of performing field monitoring methods.

DESCRIPTION OF THE BRUKER MEM

General

A diagram displaying the major components of the MEM is depicted in Figure 1. The detection unit, or actual mass spectrometer, and the associated electronics modules are housed together in a unit weighing 300 lb. with dimensions of 30 x 38 x 32 in. (l x w x h). A separate control console, connected to the MEM with a cable of varying length, has dimensions of 21 x 17 x 13 in. The complete system has been installed in a variety of vehicles, with the data for this presentation generated by a unit mounted in a Chevy Blazer 4-wheel drive truck.

The ion source is a conventional electron-impact (EI) source. A pair of filaments is included so that operation can continue uninterrupted for extended periods. The analyzer consists of a specially designed one-piece glass quadrupole with a hyperbolic metal coated surface. A mass range of 1-400 amu is provided, with a mass resolution of one amu throughout the mass range (10% valley definition). This single piece design has proven to provide exceptional rigidity and stability so as to permit the operation of the mass spectrometer under rather severe mechanical shock (6 g) conditions. Ion detection is carried out by a conventional 17-stage off-axis Cu-Be discrete dynode electron multiplier, and is coupled to a self-scaling integrating amplifier. This ion detection system has been shown to be capable of providing a dynamic range of over 10^8, with an accuracy of 15% for measurements conducted over five orders of magnitude.

By utilizing EI ionization and a quadrupole analyzer, identical to what is now used by laboratories carrying out priority pollutant analyses, the resulting mass spectra are comparable to those found in standard EI-MS library compilations. The upper mass limit of 400 amu is a consequence of power conservation requirements, and not analyzer performance. In practice, for environmental investigations this mass range is quite adequate, since for instance none of the 146 organic compounds (including internal standards and recovery surrogate compounds) comprising the Hazardous Substance List (HSL) now required for analysis under the US EPA Superfund Contract Laboratory Analysis Program (CLP) (6) contain a characteristic ion (primary or secondary) outside the MEM mass range.

The high-vacuum region of the instrument is continuously maintained at a vacuum of 10^{-6} torr by means of a 80 l/sec ion getter pump. A pump of this design, in contrast to the more common turbomolecular or oil diffusion pumps, has no moving parts and requires no external cooling. These features, coupled with its maintenance free operation, make it ideal for mobile deployment (7). The mass spectrometer is designed to operate without the need for an auxiliary roughing mechanical pump, common to most laboratory MS systems. The MEM maintains high vacuum by automatically closing the hydraulic main valve whenever power is removed or a major fault is detected. At the completion of manufacturing and testing, the MEM is initially rough-pumped at the factory with a standard mechanical pump, prior to engaging the ion getter high vacuum pump. Once this is accomplished, the high vacuum state should remain intact barring a need to access the detector region. In practice, it is not unusual for a unit to be under daily operation in excess of a year between rough pumps. Test units left idle (power removed) have held vacuum for over 6 months.

A separate housing contains the complete set of mil-spec circuit boards responsible for controlling the MEM. Operation of the MEM is conducted through a separate control console containing a keyboard, printer, video monitor, and push-button controls. Two microprocessors provide digital control of all mass spectrometric functions and temperatures. A continuously operational supervision program (SELF-MONITOR) can detect more than 80 instrumental errors or malfunctions. All the errors are counted and logged, and serious errors are immediately displayed to the operator. Also, a check program for all the essential operating functions can be manually initiated. Moreover, built in diagnostic programs allow for the measurement of 30 analog values (temperatures, voltages, currents) and over 100 digital switching states allowing for detailed trouble-shooting in the field.

Inlet System

The gas inlet system, Figure 2, controls the direction and nature of the gas flow to the inlet membrane interface. The inlet membrane, housed in the heated (150 C) main valve, serves to isolate the high vacuum region of the mass spectrometer from the sample gas stream. Organics pass selectively through this membrane into the ion source, preferentially excluding the lighter components of air. Normally whenever the system is on, the carrier gas pump is on, allowing for sample flow through the sampler line (or optional GC unit) and past the inlet membrane surface. Alternatively, if the sample line gets contaminated the entire gas inlet manifold may be backflushed by turning off the carrier gas pump and switching on the back-flush pump. Provision has also been made in this inlet system for the automatic delivery of a mass calibrant compound for tuning purposes. The operator can easily change the inlet membrane, air/surface sampler, and capillary GC unit within a few minutes in the field, without breaking high vacuum.

Sampling Systems

The direct air/surface sampler consists of a flexible, heated tube 10 feet long with a diameter of 2 inches. The sampler head is comprised of a silicon membrane mounted on a nickel screen. Directly behind the membrane lies the actual sample transfer line, a 3.5 m fused-silica SE-54 bonded capillary GC column of 0.32 mm internal diameter. The sampler is mated to the gas inlet manifold by means of a threaded quick release coupling, with the end of the GC column located close to the inlet membrane. Both the head and transfer line can be separately temperature programmed from ambient to 260 C, and ambient to 240 C, respectively. At typical operating temperatures the air flow through the sampler line is about 2.0 ml/min.

This air/surface sampler has been found to allow for the direct sampling of ambient air, water, and soil for a wide range of organic compounds. For instance, sampling can be conducted by pressing the head directly against soil, held over a monitoring well or sample containing jar, or alternatively, pressed against a clean surface (glass, aluminum foil, Teflon, etc.) to which an aliquot of a solvent extract of a sample has been deposited. It is this flexibility of alternate sample introduction avenues that has permitted the MEM to solve quickly many problems related to field based sample preparation requirements.

The capillary GC oven accessory is a recent addition to the MEM and was developed to provide extended analytical capabilities as compared to the rapid air/surface sampler. The GC oven is mated to the mass spectrometer using the coupling shared by the air/surface sampler, with exchange of these units normally carried out in a few minutes. The GC unit, Figure 3, has been optimized in terms of size, weight, and power requirements, and is controlled and powered by the MEM electronics. Among the unique features of this GC is an injection port designed for automatic thermal desorption of sorbent filled sampling tubes. Glass tubes typically filled with Tenax or Tenax/charcoal, are utilized to trap volatile organics directly from ambient air or, alternatively, from water or soil samples through a purge and trap step. By placing these sample tubes in the heated injection port, a direct transfer of the desorbed analytes can be made to the head of the capillary column. The subsequent GC-MS run may then be carried out under an isothermal or temperature ramp program, followed by a cooling phase in anticipation of the next analysis. During the actual GC-MS acquisition, the sorbent tube is automatically cleaned via a backflush of cleaned air. Additional options available for this GC unit include a direct (on-column) injection port and an auxiliary nitrogen carrier gas delivery system. Surprisingly, very good results have been obtained with just clean air as GC carrier gas - including hundreds of injections onto a DB-624 bonded column over several months of use.

MEM Data System

A key feature of this field instrument is the unique approach taken for automatic target compound monitoring, which permits continuous sampling with a minimum of operator intervention. A typical screen display during one of the main acquisition programs , AIR MONITOR, is shown in Figure 4. In AIR MONITOR, up to 22 compounds may be simultaneously monitored, through selected ion monitoring (SIM) acquisition scans of 1 to 4 ions per compound. When the instrument observes the presence of the target ions in the correct ion abundance ratios, the screen will automatically display the name of the compound observed. Along the x-axis of the screen reproduced in Figure 4 are the ion groups for the various target compounds selected for analysis (compounds A - J). Ion current is plotted along the y-axis, on a logarithmic basis, necessary for the enormous dynamic range encompassed in potential environmental analyses. At any point in time, a complete mass spectrum can be obtained over a prescribed mass range by pressing a key labeled SPECTRA on the control unit. A more detailed discussion of the AIR MONITORING identification and quantitation software can be found in a companion paper (8).

External PC Compatible Data System

Additional data acquisition, storage, and manipulation capabilities have recently been added to the MEM through interfacing a PC compatible microcomputer. As portability/ruggedness was also a criteria for this hardware addition, the Compaq Portable III system has been selected, equipped with 1 Mbyte RAM and a 40 Mbyte hard drive. The external data system is particularly useful for acquiring full-scan capillary GC-MS runs, as a data storage problem for this type of application exists with the limited memory capabilities of the internal MEM data system. The development of automated quantitation software, a mainstay of todays environmental GC-MS laboratory, is under development for implementation on the Compaq/MEM system.

APPLICATIONS TO HAZARDOUS WASTE SITE INVESTIGATIONS

Direct Air/Surface Sampler

The determination of the nature and extent of contamination by petroleum products and wastes represents a significant per-centage of the total environmental pollution problems facing the industry. We have found the air/surface sampler to be a quick, effective means of screening large numbers of soil and water samples for relative hydrocarbon levels, with no sample preparation required. For instance, tracking the impact of a leaking underground gasoline tank was possible by programming the MEM to continuously monitor for the target compounds benzene, toluene, total xylenes, and in addition, total aliphatic hydrocarbons. Since a combination of shallow soil gas wells, soil borings, and groundwater monitoring wells were featured in the sampling program, results from a large number of measurements had to be provided in real-time. Figure 4 shows a typical screen display, updated every 5 seconds, for gasoline components from a water headspace sample. Others have reported an additional advantage of on-site analysis of volatiles with this sampler, namely that the field results are invariably higher in concentration to that reported by the off-site analytical laboratories, demonstrating rapid sample degradation to be occurring (9).

This sampler has also been found to be quite effective in the detection and identification of commercial polychlorinated biphenyl mixtures (Aroclors) in soil. For these semi-volatile components, the SURFACE-MONITOR MEM program was employed, which permits a discrete "injection" to be made by placing the heated sampler head (260 C) directly into the suspect soil for 30 sec, while keeping the SE-54 capillary transfer line at a relatively low temperature (150 C). After this initial concentration phase, the GC column is quickly ramped to 220 C and data acquisition is carried out for a period of 200 sec. Under these conditions the PCB isomers are introduced into the MEM and monitored by ions characteristic of each individual PCB chlorination level. Figure 5 is an example of the MEM results from analysis of a soil sample certified to contain 35 ppm of the mixture Aroclor 1242 (ERA Inc., Arvada, CO). The relative concentrations of the different PCB chlorination levels is a characteristic of each commercial Aroclor mixture (10) and can be an effective means of identifying the actual Aroclor product observed. Since no time-consuming and expensive solvent extraction steps are required to obtain these results in the field, this appears to be an ideal approach to screening large numbers of soil samples on a timely and cost-effective basis where the data is needed most - with the sampling crew. Other classes of semi-volatile compounds, in particular several common pesticides, polyaromatic hydrocarbons (PAH), and polychlorinated dibenzodioxins (11) have also proven to be amenable to this approach.

Applications dictating the need for the GC oven accessory are those instances where the complexity of the matrix necessitates a more effective GC separation (30 m versus 3.5 m column, selection of unique bonded phase to affect separation, etc.) and/or the attainment of lower detection levels through preconcentration steps. For example, we have found the MEM reliable for the routine screening of water for common volatile organics at the 50 to 100 ppb level when using the direct air/surface sampler. In a recent application, quantitation approaching the sub ppb level was requested for the aromatics benzene, toluene, ethyl benzene, and xylenes (BTEX) in surface and groundwater. This was accomplished with field purge and trap concentration on a 100 ml water sample, using a commercially available purge vessel (Alltech Assoc., Deerfield, IL), Tenax sorbent tubes, and ambient air as purge gas. Figure 6 shows the total ion current chromatogram resulting from a sample run with the target compounds spiked at 5.0 ppb and separated on a 30 m DB-624 column (J&W Scientific). For this program, rigorous instrument calibration was carried out using an internal standard spiked at 50 ppb into all blanks, calibration, QC, and actual field samples. A typical calibration curve obtained by this method is presented in Figure 7. Using a similar thermal desorption GC-MS approach, volatile organics trapped from soil and ambient air (Tedlar bags) have also been monitored in the field by the MEM. On occasion it has also proven useful to analyze sample solvent extracts of semi-volatile mixtures on the GC, by injection via an empty glass tube in the thermal-desorption injection port, or alternatively, using the direct on-column injection port.

CONCLUSION

An instrument capable of providing unambiguous GC-MS data in the field, without burdening field sampling crews with providing complex support and sample preparation facilities, has been shown to be an effective tool for the characterization of hazardous waste sites.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Jochen Franzen and Dr. Alex Loudon, of Bruker-Franzen Analytik GmbH, for their assistance.

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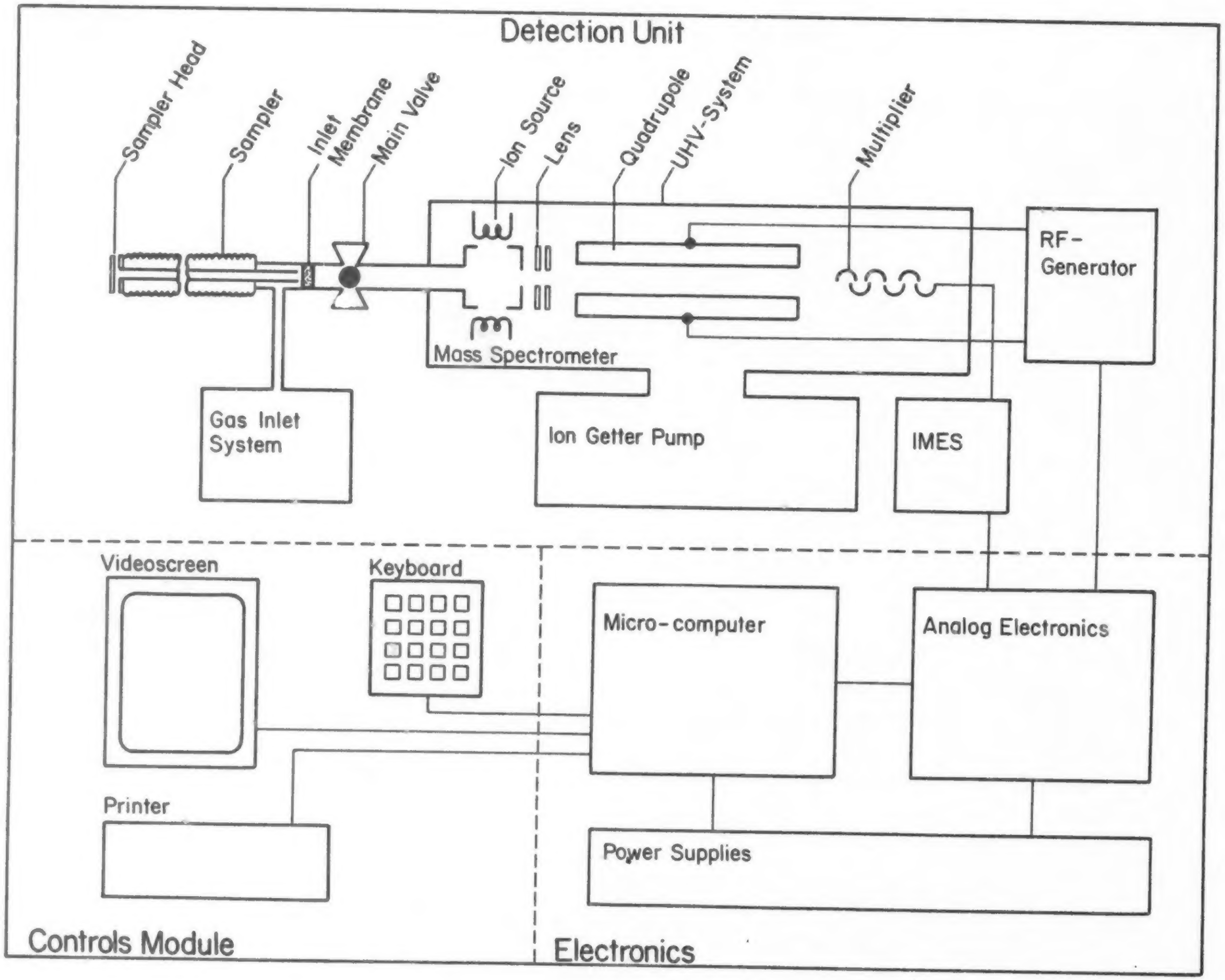

Detection Unit
Sampler Head
Sampler
Inlet Membrane
Main Valve
Ion Source
Lens
Quadrupole
UHV-System
Multiplier
RF-Generator
Mass Spectrometer
Gas Inlet System
Ion Getter Pump
IMES
Videoscreen
Keyboard
Micro-computer
Analog Electronics
Printer
Power Supplies
Controls Module
Electronics

FIGURE 1. MAJOR COMPONENTS OF THE BRUKER MOBILE ENVIRONMENTAL MONITOR.

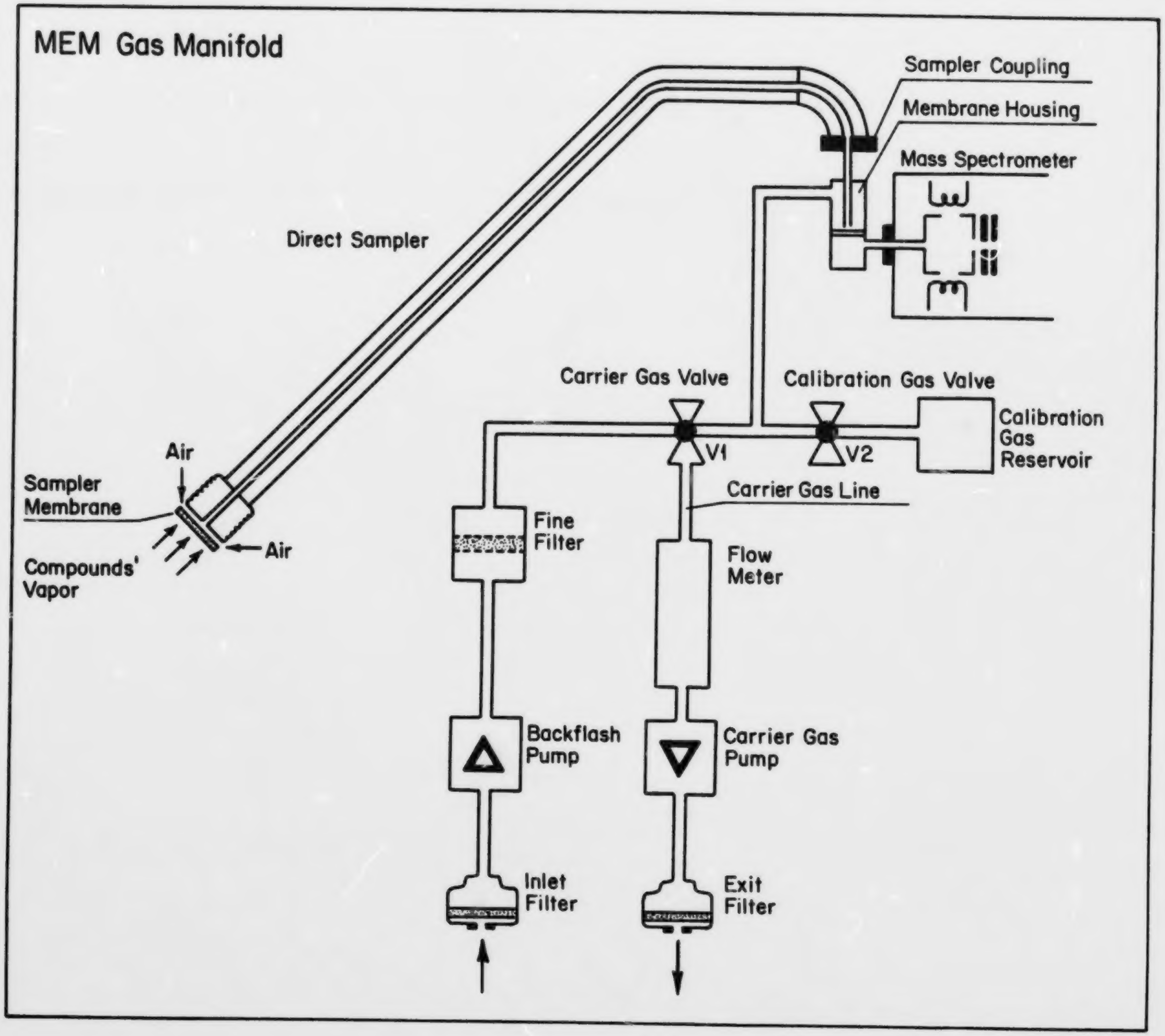

MEM Gas Manifold
Sampler Coupling
Membrane Housing
Mass Spectrometer
Direct Sampler
Air
Sampler Membrane
Air
Compounds' Vapor
Carrier Gas Valve
Calibration Gas Valve
V1
V2
Calibration Gas Reservoir
Carrier Gas Line
Fine Filter
Flow Meter
Backflash Pump
Carrier Gas Pump
Inlet Filter
Exit Filter

FIGURE 2. MEM GAS INLET SYSTEM.

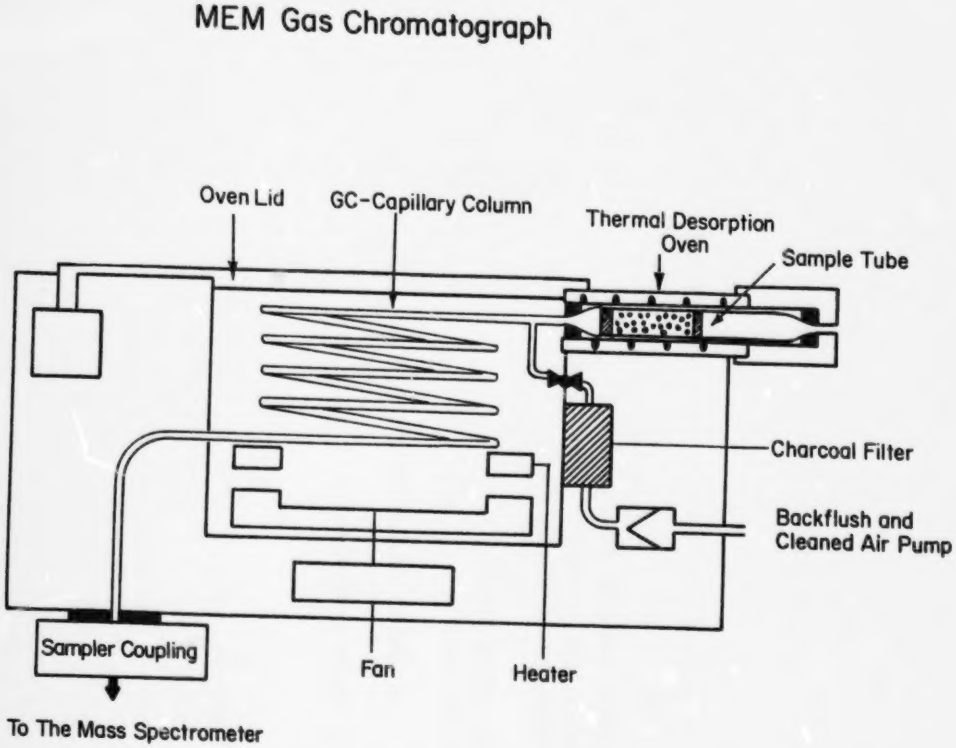

MEM Gas Chromatograph
Oven Lid
GC-Capillary Column
Thermal Desorption Oven
Sample Tube
Charcoal Filter
Backflush and Cleaned Air Pump
Sampler Coupling
Fan
Heater
To The Mass Spectrometer

FIGURE 3. MEM CAPILLARY GC OVEN ACCESSORY.

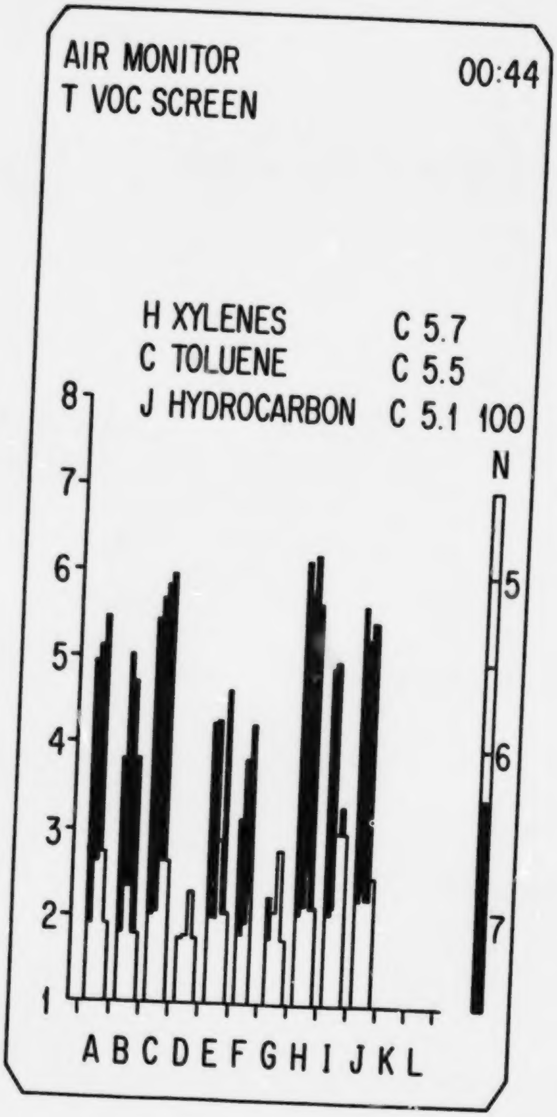


FIGURE 4. EXAMPLE OF THE MEM AIR MONITOR REAL-TIME VIDEO DISPLAY.

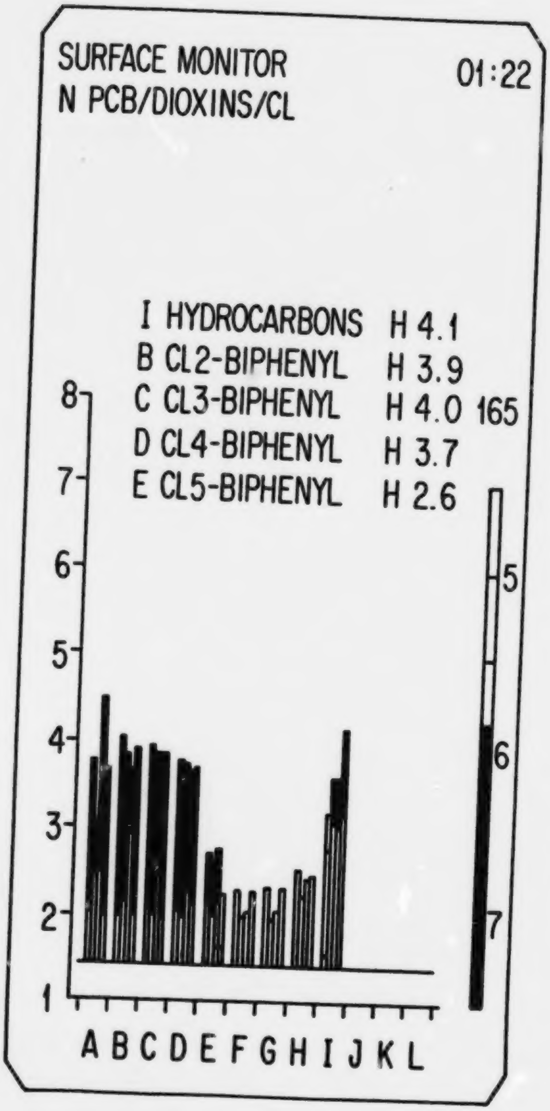


FIGURE 5. DETECTION OF PCB (AROCLOR 1242) IN SOIL BY THE MEM SURFACE MONITOR PROGRAM.

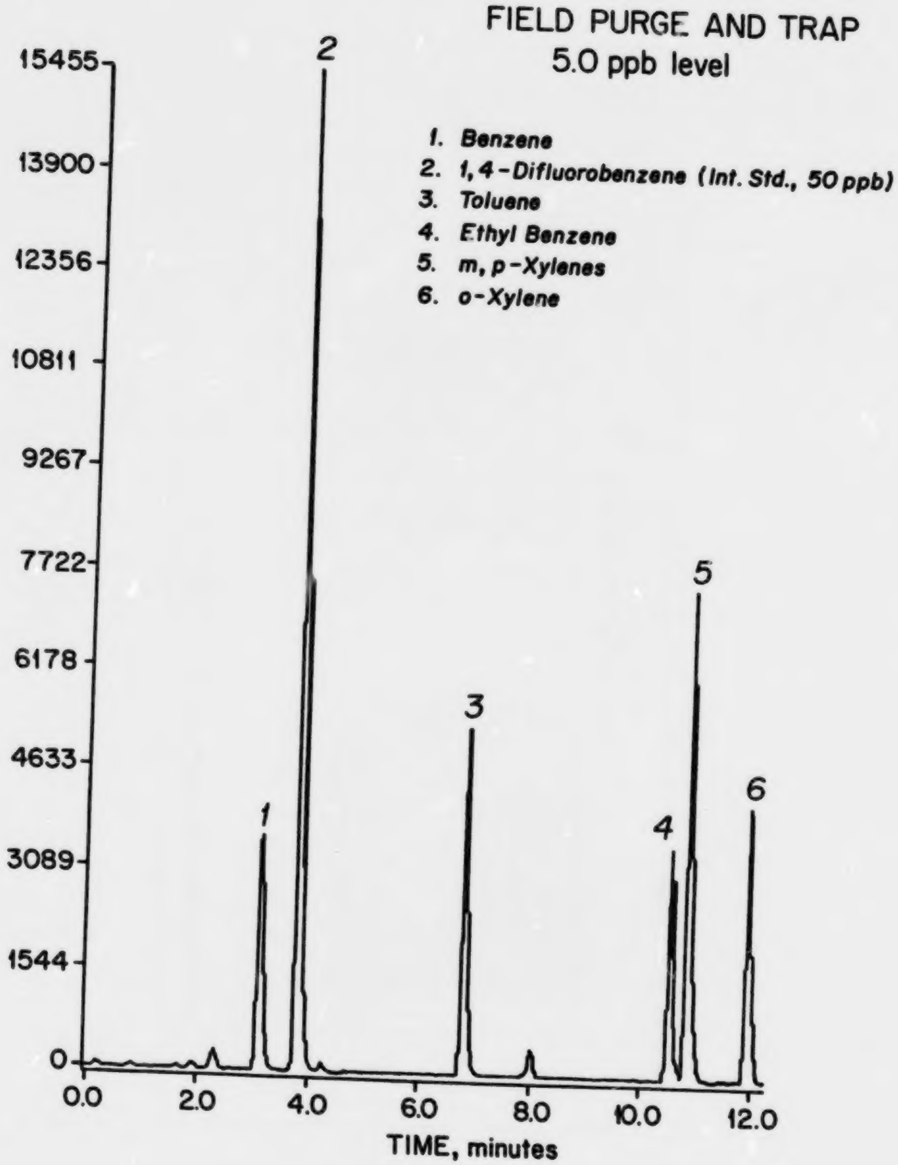


FIGURE 6. TOTAL ION CURRENT PROFILE FROM THE MEM ANALYSIS OF WATER SPIKED AT THE 5.0 PPB LEVEL OF BENZENE, TOLUENE, ETHYL BENZENE, AND XYLENES.

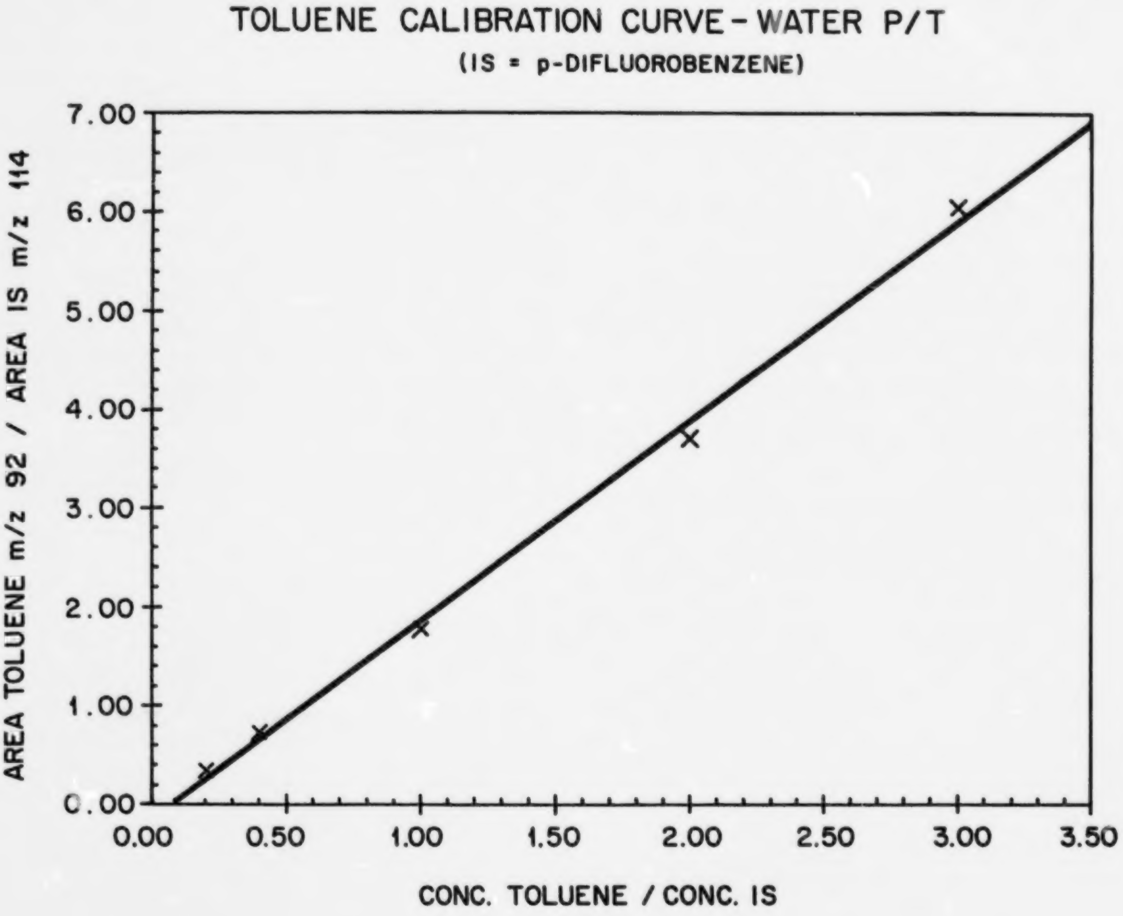


FIGURE 7. CALIBRATION CURVE FOR TOLUENE ANALYZED BY PURGE AND TRAP/THERMAL DESORPTION GC-MS ON THE MEM.

DISCUSSION

JONATHAN NYQUIST: Did you say you're using charcoal as a prefilter in the purge and trap for the air samples?

THOMAS TRAINOR: That's one filter you can use.

JONATHAN NYQUIST: Doesn't that take out some of the organics right there on the charcoal, before it ever gets to your instrument?

THOMAS TRAINOR: With the field purge and trap, you do not want to introduce volatiles from the ambient air into the water or soil sample, contained in the purging vessel. In the lab, you would use nitrogen or helium as a purge gas. We have eliminated that and used air, but you can't assume the air that's surrounding your waste site is clean. So you're prefiltering it.

If you're talking about the flexible membrane liner situation, that system will identify the potential problems with your data. Where it differs from the experts, it will provide an explanation. Say the liner is not resistant, and provide the reasons if it generates an answer. Then it's up to the reviewer to bring these problems up with an expert.

JONATHAN NYQUIST: You mentioned in your criteria of expert systems, about meeting a consensus among the experts. At hazardous waste sites, we rarely have that, particularly because site-specific issues often take control. Do you think we'll be able to use them at different hazardous waste sites?

DANIEL GREATHOUSE: I think you'll be able to use them for specific issues at hazardous waste sites. I don't think you'll ever be able to use one that will just take the place of a Remedial Project Manager at a hazardous waste site or a contractor at a hazardous waste site.

For example, we have one expert systems program at hazardous waste sites to help screen technologies for cleaning up sites. It's simply a screen. All it does is select from 35 technologies the ones that are most feasible to use for site clean up, perhaps ten or six. It then focuses the attention of the reviewer on those, and it can get more information about any of those appropriate.

I don't think they will ever get to the point of replacing an expert. There are too many unique situations that you just cannot address with an expert system.

From our experience, the primary application of expert systems are for the more routine problems. These are 80 out of 100 problems that do not have all these unique characteristics.

The unique problems, which require special considerations extrapolating from other fields, or whatever, are ones that will never be addressed by expert systems.

EXPERT SYSTEMS TO ASSIST IN EVALUATION OF MEASUREMENT DATA

Daniel G. Greathouse
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268

INTRODUCTION

The Agency expends a significant proportion of its budget to measure levels of contaminants or effects of contamination in the environment. In addition it mandates that other organizations, primarily private companies, expend considerable resources to provide measurement data to the Agency. This requires that decisions be made concerning appropriate sampling methods and analytical techniques and results in huge volumes of measurement data that must be evaluated and interpreted by Agency personnel. Concerns such as extent of contamination, potential health risks due to the contamination, and likelihood of adverse health consequences by introduction of new chemicals into the market place are just a few of the decision areas based on these data. Clearly the potential health consequences and economic implications of these evaluations and interpretations are very significant. Hence it is very important that the best expertise be brought to bear on these decisions. The purpose of this paper is to review the development of expert systems by U.S. EPA to assist in evaluation of measurement data.

The expertise required to adequately perform the necessary evaluations and interpretations of measurement data depends in part on such things as the media that are measured, the matrix of compounds in the media, and the nature of the measurements. Typically, satisfactory evaluation and interpretation will require knowledge concerning the analytical methods, sampling procedures, underlying chemistry and/or biology, effects of the matrix of compounds in the samples, etc. This knowledge will be gained partly from formal education, but much will be based on extensive relevant experience.

Scarcity of qualified personnel to design measurement studies and to evaluate and interpret the resulting data is typical in the Agency. This problem is accentuated since these decisions have largely been delegated to the EPA Regional Offices and states. Expert systems are tools that have the potential to make available the expertise required to make these decisions. These systems will make it possible to multiply the talent of experts.

An expert system is an automated process which incorporates the judgement, experience, rules of thumb, and intuition used by a human specialist to emulate that specialist's problem solving ability. Generally, the knowledge of specialists is stored in a computer in the form of facts and decision rules although many, more complex representations are available. Expert systems have several characteristics which differentiate them from conventional software. Whereas conventional computer programs rely on numeric algorithms as the basis for their operation, expert systems are characterized by an emphasis on symbolic processing, logical inferencing, and pattern matching. Most expert systems contain facilities which allow the user to obtain an explanation concerning why a question was asked and/or to obtain clarification for a particular question if the user requires more information. In addition, the user is often supplied with the reasoning employed in reaching a conclusion. Expert systems are interactive; they do not run and calculate so much as they aid thought and offer advice.

A recently increased interest in the development of expert systems has brought to market software tools known as expert system shells. Basically, a shell simplifies the development of expert systems by providing a programming environment with a built in library of functions for common tasks such as rule generation, definition of objects, and interfacing with the user. This means that the builder of the system can concentrate on the acquisition of knowledge rather than on low level programming issues. The arrival of shells in the software marketplace is in part responsible for the success of many expert system projects.

There are a myriad of shells available to today's developers. Each shell has a different set of features and capabilities. For instance, some shells allow only text to be used for user prompts and output while other shells are more versatile. Some provide easy access to external data bases. Others provide the capability to attach the computer to certain measurement devices with readings displayed and control functions available graphically on the computer monitor.

Of course, the cost of a shell is usually indicative of the breadth of features although competition in this market is increasing. For some projects a low cost/capability shell will suffice while in other environments advanced features are well worth their price. In general, shell selection is an important consideration which must be made with respect to the problem domain and the desired system functionality.

REVIEW OF EXISTING SYSTEMS

Some of the systems being developed to provide assistance in the measurement area will be summarized. For more information concerning the cited expert systems see the list of contacts provided in the appendix.

Flexible Membrane Liner System (FLEX)

Flexible membrane liners are plastic sheet materials that are used as moisture/liquid barriers in a landfill. They are placed under wastes to prevent leachate from leaking into the groundwater and on top of the wastes to keep water from entering the wastes. Typical plastic formulations for these liners are polyvinyl chloride (PVC), high density polyethylene (HDPE), and chlorosulphonated polyethylene (CSPE). Before one of these materials can be used as a liner for a hazardous waste land disposal site, the Agency requires that it be tested for chemical resistance to the anticipated leachate from the landfill. A series of physical property measurements must be performed on the liner material after exposure to the anticipated leachate for prescribed periods of time. The test protocol is known as the Method 9090 test. An expert system, known as FLEX, has been developed to assist in evaluating and interpreting these physical property measurements. The rules are based on the input of 6 flexible membrane liner specialists. In essence the system determines if the data is adequate to fit a quadratic model and if so uses the model to determine if the predicted trend (change in the physical property measurements) over time exceeds the limits prescribed by the experts. Standard statistical methods are used to examine the data and to fit the quadratic model. The system is written in Arity Prolog for application on an IBM PC/AT class micro computer. Currently the system is being field tested.

Geophysics Expert System

This system is being designed to aid Superfund managers in selection of appropriate geophysical measurement methods. Different measurement scenarios are recommended based on the user identified purpose of the measurements. For example the system proposes a measurement scheme for situations when the goal is to assess extent of contamination as part of a site assessment. In addition to identifying the purpose of the measurements the user is also requested to supply general information concerning the site. The first version of the system is currently being reviewed and development of the second is scheduled for completion by early 1989. A follow-up will be initiated when funds become available. Each successive version is being designed to address a wider array of decision scenarios. The system is being developed in Basic for application on an IBM compatible micro computer.

Quality Assurance/Quality Control

Systems are being developed to improve the quality of measurement data produced by laboratories and to document this improvement. A system is being developed by EPA Headquarters to aid in implementation of the EPA developed data quality objective procedures/standards when designing a laboratory measurement program. More specifically it will provide three levels of assistance, namely (1) define the decision, (2) specify the information and confidence levels needed to make the decision, and (3) design a sampling plan to gather the information.

Radian Corporation has developed two prototype systems to provide sampling assistance. The smaller one aids in selection of the appropriate analytical method that will yield the desired level of accuracy for the compounds to be measured. If no method will provide the desired level of accuracy the user is supplied with a warning and information concerning the most accurate method available. Each method description includes procedures, specifications of number of QC samples (blanks and spikes, replicates and duplicates) to be taken, and a reference to the EPA document from which the text was drawn.

The larger, more complex, system is designed to aid in defining quality assurance and quality control sampling requirements. The system questions the user to determine the kind of errors to be controlled, for example; sampling or laboratory errors, biases or random errors, within or between day variations, and so on. Based on this, the system recommends types of QC samples to be sent to the laboratory, i.e.,. spikes, duplicates, replicates. The user picks recommended kinds of QC   s, one at a time, and looks at them quantitatively. Based on how much variation is acceptable, how many samples are in a set, how rapidly (number of days of sampling) drift is to be recognized, and the desired certainty of recognizing drift if it occurs within a specified time frame, the program will recommend the number of QC samples to be taken per day. Alternatively, given the other parameters, it will derive the level of certainty from the number of samples.

This list of expert systems should not be considered as an inclusive list of all systems that have been designed to assist those responsible for decisions concerning measurement processes. Instead they illustrate the types of systems that can be and are being developed in the area.

DISCUSSION

Measurement of contaminants in the environment requires knowledge concerning a wide range of issues. Some of this information is contained in textbooks, scientific literature, and government reports. Some of the general rules or principles are only known by those who have extensive experience in the field. Expert systems provide an excellent means of compiling and synthesizing this knowledge and expertise in a form that can be accessed by persons with less training and experience. It should be emphasized however, that these systems can not replace the expert: they can however, extend the expert s knowledge. They can not provide advice concerning issues that can not currently be resolved by an expert or knowledgeable person in the field. For example a system can not be developed that will give advice concerning a new instrumentation method that has not yet been conceived or tested. The primary application is in the more routine situations which experts can resolve in a few hours to a few days.

There are a number of measurement and instrumentation issues that could be used as the focus for expert systems development. If the goal of developing an expert system is to aid other decision makers it is important that the effort be successful. Success is determined by three related criteria. First the system must accurately represent/ emulate the decision processes used by knowledgeable persons in the field. Second, the system must also produce sufficient increases in decision efficiency and quality to warrant the costs for development, maintenance, and user training and support. Finally, the systems must be accepted and employed by the targeted user community. The following questions should be asked before initiation of an expert system development effort to assess the potential for success:

1. Do experts/knowledgeable persons exist who are available and willing to serve as resources in formulating the decision rules?

2. Is there consensus among the experts and/or user community concerning the decision rules appropriate for the application area addressed by the system?

3. Does the system address a definable need of the targeted user community and will knowledgeable persons from the user community participate in each stage of the development process?

4. Can the knowledge/expertise in the subject area be adequately represented with available software and hardware and will the targeted user community have the necessary input information for the system to provide meaningful advice?

5. Can a definite plan be developed and resources allocated for regular maintenance of the knowledge base and software and for providing user support and training to the target user community?

6. Are decisions in the selected area made often enough to justify undertaking software development and maintenance?

If these questions are answered in the affirmative then the potential developer must explore the scope of the problem to be addressed. If the problem is too simple an expert system will not represent a high enough payoff to justify the time and money spent developing the system. If the problem is too complex the development task will quickly become overwhelming. A rough estimation of problem scope can be measured by the time it takes an expert/knowledgeable person to reach a solution. In general an expert should be able to arrive at a decision in between one to eight hours. Additionally, the decision should be based upon implicit or explicit rules and criteria rather than strictly upon common sense. Consistent responses among decision makers and over time are also desirable features.

CONCLUSION

Expert systems offer the potential of synthesizing the knowledge and thought processes of the instrumentation experts in a form that can be used by less knowledgeable persons. In essence these systems offer an excellent mechanism for technology transfer. Some expert tools have been developed to aid in measurement related decisions. There appears to be a definite need for systems to aid specifically in instrumentation decisions and in the array of measurement issues that must be considered by the Agency and the regulated community. The apparent need for these systems, as perceived by the experts and developers, should not, however, be used as the basis for initiating development of an expert system in the area. The importance of input from the targeted user community and a thorough evaluation of system costs and benefits prior to system design and code development can not be over emphasized. The targeted user community must be actively involved during each stage of system development starting with the conceptualization stage and proceeding through the final stages of testing and maintenance of the production system. Poorly designed and maintained systems and/or unused systems are not only expensive, but tend to result in a loss in faith for a technology that offers significant opportunities to improve the efficiency of decision makers and enhance the quality of their decisions.

APPENDIX

CONTACTS FOR FURTHER INFORMATION CONCERNING THE CITED EXPERT SYSTEMS

FLEX (Flexible Membrane Liner System)

Daniel G. Greathouse
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
26 W Martin Luther King Drive
Cincinnati, OH 45268

Geophysics Expert System

Aldo T. Mazzella
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
P.O. Box 15027
Las Vegas, NV 89114

Data Quality Objectives Advisor

Dean Neptune
Quality Assurance and Monitoring Support
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

Quality Sampling and Analysis

Lawrence Keith
Radian Corporation
P.O. Box 9948
Austin, TX 78766

DISCUSSION

W.F. ARENDALE: We've been talking about many of the problems and costs of transferring from the research laboratory to the field. I am convinced that expert systems have a place. But the big problem is that systems won't transfer data. There must be something done to transfer data from one to the other.

As you monitor expert systems, do you see them being programmed directly in LISP or PROLOG or a higher level language. Is there a collective effort to bring this technology to the field?

DANIEL GREATHOUSE: The field is evolving very rapidly. The systems are being developed, and some of them are in the languages, some of them are using shells. That causes a real problem with trying to get compatibility among them.

Here's one example of trying to do something about it, in the QA/QC area. We did a needs assessment among our regional offices and found that there was a real need in that area for advice on a number of different issues. There are about eight systems being developed, and as you would expect, they are not compatible. We are trying to pull that information together and at least provide access to the different systems, or we're trying to work out some way to unify the information in that area.

One of the problems is that expert systems are being developed by a number of independent groups that aren't related. How do you get compatibility among the products that come out? I'm not sure.

That's one of the reasons that there was an initiative approved by EPA for expert system development to respond to regional office needs. The objective of the initiative is to pull together systems in various areas, and make them compatible and more usable for the user community.

JONATHAN NYQUIST: I think we have all seen some of the medical expert systems that do the diagnosis and help the doctor consider possibilities he hadn't looked at, or might not look at otherwise. I don't think we would like to see that expert system take the place of the doctor, and I guess that is one of the things that makes me a little worried. When there is a lack of trained personnel, aren't we giving them a loaded gun with these expert systems?

DANIEL GREATHOUSE: I don't think so. First, you have to realize that those decisions are going to be made by the person without training anyway. The idea is to try to provide available information to them, as easily as possible, and in a way that they will not use the information in place of the decision maker, but as a screen.

A POSITIONING AND DATA LOGGING SYSTEM FOR SURFACE GEOPHYSICAL SURVEYS

Jonathan E. Nyquist
Health and Safety Research Division
and
Michael S. Blair
Instrument and Controls Division

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

ABSTRACT

The Ultrasonic Ranging and Data System (USRADS) developed at ORNL is being adapted to work with two commercially available geophysical instruments: a magnetometer and an EM31 terrain conductivity meter. Geophysical surveys have proven an important preliminary step in investigating hazardous waste sites. Magnetometers and terrain conductivity meters are used to locate buried drums, trenches, conductive contaminant plumes and map regional changes in geology. About half the field time of a typical geophysical investigation is spent surveying the position of the grid points at which the measurements will be made. Additional time is lost and errors may be made recording instrument values in field notebooks and transcribing the data to a computer.

Developed for gamma radiation surveys, the USRAD system keeps track of the surveyor's position automatically by triangulating on an ultrasonic transmitter carried in a backpack. The backpack also contains a radio transmitter that sends the instrument's reading coincident with the ultrasonic pulse. The surveyor's position and the instrument's reading are recorded by a portable computer which can plot the data to check the survey's progress. Electronic files are stored in a form compatible with AutoCAD to speed report writing.

INTRODUCTION

A number of surface geophysical methods developed for oil and mining industry applications have been adapted for the investigation of hazardous waste sites, for example: magnetic field intensity, resistivity, time domain electromagnetics, and frequency domain electromagnetics (1,2). While formerly the geophysical prospector used a magnetometer to search for iron ore, now the same instrument may be used to locate buried drums of toxic waste (3,4). But the goal of geophysical surveying remains the same: to learn as much as practical about the subsurface before going to the expense of drilling. Often fewer wells are required to characterize the subsurface as the geophysical data can be used to choose the best well sites and to interpolate between wells. In some cases, such as searching for buried drums, a geophysical survey can save thousands of dollars in hit-or-miss excavation efforts.

While geophysical surveys are relatively fast and inexpensive, time and money are lost while surveyors set up the measurement grid. Additionally, although most modern geophysical instruments have a built-in data logger and can dump the survey data to a portable computer at the end of a survey, there is no way to view the collected data while the survey is in progress. Often the grid lines turn out to have been too widely spaced, or the grid did not cover a large enough area; as a result, the surveyors must be brought back to the field to refine or extend the grid.

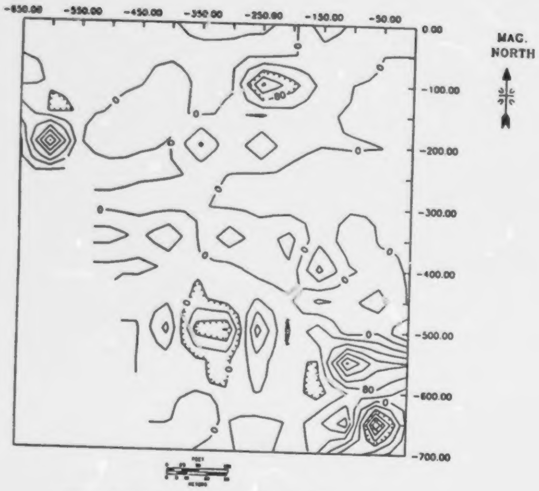
The need to expand or refine a measurement grid and to analyze the data while the survey is in progress are common to all field surveys. The same problems arose, when as part of the Department of Energy's Uranium Mill Tailings Remedial Action Project (UMTRAP), ORNL was requested to survey, in three years, 8,000 properties where presence of uranium mill tailings were suspected. To save time and money ORNL developed a technology to automate much of the survey process and provide tabular and graphical data display in the field or in the office for report generation. This technological development is called the Ultra Sonic Ranging and Data System (USRADS) (5).

Our recent work has focused on interfacing two geophysical instruments, a proton procession magnetometer (Omni IV) and an electromagnetic terrain conductivity meter (Geonics EM31) with the USRADS. This work is still in progress. In this paper we will describe the application of the two geophysical instruments and the USRADS separately, and the work which being done to combine them.

CASE STUDY: EVAPORATION PIT AT DYESS AIR FORCE BASE

An evaporation pit at Dyess Air Force Base in Abilene, Texas received liquid waste from the late 1950's to the late 1970's, when it was backfilled and abandoned. The pit's approximate areal dimensions are 45 x 30 m (150 x 100 ft) from base records. After the pit was closed, base personnel continued to use a buried 38,000 liter (10,000 gal) railroad tanker car to the east of the evaporation pit as a liquid waste repository until 1982. The tanker has since been removed.

Although it was believed that only liquid waste was disposed of at the site, a preliminary inspection found crushed drum fragments, railroad spikes and other metal debris on the surface. We decided to use a magnetometer to check for buried metal as well. A rectangular grid consisting of 194 points on a 15 m (50 ft) spacing took two days to survey. The region in the southwest corner was not surveyed because small trees interfered with sighting the transit. A team of two completed the actual magnetometer survey in a single morning. The results show strong dipole anomalies (paired lows and highs, Figure 1). For each pair, the buried source, probably one or more 208 liter (55 gal) steel drums, is located about halfway between the adjacent positive and negative peaks. Notice that the peaks are always located on a grid point. This is because the anomalies are smaller than the grid spacing. The actual buried object producing the anomaly may lie as much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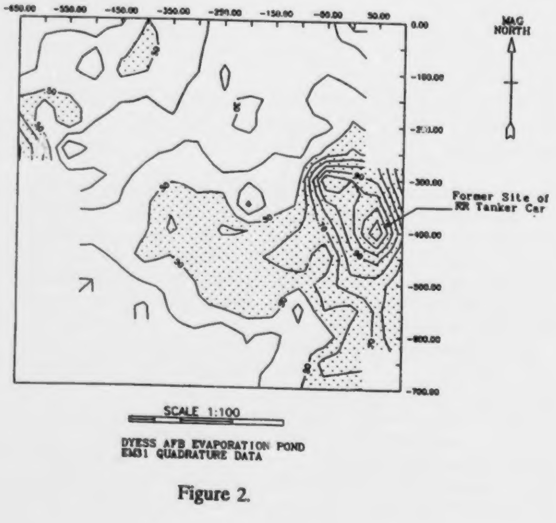
-300.00
-400.00
-500.00
-600.00
-700.00
MAG.
NORTH
0
-80
80

DYESS AFB HARDFILL #1 AND EVAPORATION PIT
MAGNETIC GRADIENT DATA. CI=40 GAMMAS/M

Figure 1.

The terrain conductivity data (Figure 2) adds to the picture formed from the magnetic gradient contours. This survey took two people an afternoon. While the magnetometer responds only to the total mass of ferrous metal, the terrain conductivity meter responds to anything conductive which depends on the conductivity and surface area. It is less affected by the small buried metal, but shows a strong anomaly centered on the former location of the buried railroad tanker car and a plume appears to have formed to the west. Sixteen grid points were surveyed around the tanker car, extending the grid to the east and verifying that the tanker car was the source.

If time had permitted, more measurements would have been made to the east of the tanker car to completely map the plume. We later learned that the our survey had caught only the very edge of the evaporation pit (northwest corner of Figures 1 and 2); most of the survey grid was over a hardfill area where metal scrap had been dumped. The grid should have been expanded to the west as well. Such surprises in the field are common and illustrate that surveying the grid point locations and reducing the geophysical data handicap an otherwise fast, effective and inexpensive reconnaissance. A way is needed to analyze the data in the field and adjust the survey lines, without mobilizing the field crew a second time.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-300.00
-400.00
-500.00
-600.00
-700.00
MAG
NORTH
Former Site of
RR Tanker Car
SCALE 1:100

DYESS AFB EVAPORATION POND
EM31 QUADRATURE DATA

Figure 2.

ULTRASONIC RANGING AND DATA SYSTEM (USRADS)

System Operation and Setup

Real-time analysis of the data is a major advantage of the USRADS. As the surveyor walks the property, an ultrasonic crystal in the surveyor's backpack is pulsed each second and the data from the survey instrument are transmitted to the computer by radio. Each second, the computer reads the time-of-flight data from stationary receivers placed in the survey area, triangulates the surveyor's location, plots the surveyor's location on the computer screen, and stores all raw data. By plotting the surveyor's location each second, the computer operator can view the surveyor's coverage of the property at any time during the survey. In addition to plotting the surveyor location, the computer highlights any data point that exceeds a threshold entered by the operator, so that any areas of concern are identified on the display, to ensure that sufficient data have been obtained to characterize that area.

The system setup takes only about fifteen minutes. Stationary receivers are placed so that the surveyor is in view of at least three of them from any location on the property (Figure 3). Only the first few receivers need to be located by a surveyor; once the stationary receivers have been placed on the property, they are used to calculate the speed of sound and the locations of the remaining stationary receivers are computed automatically.

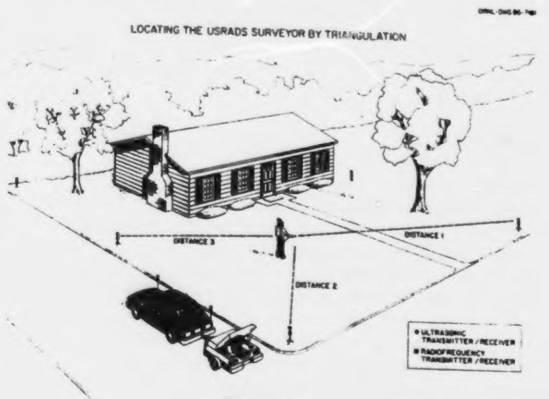
LOCATING THE USRADS SURVEYOR BY TRIANGULATION
DISTANCE 1
DISTANCE 2
DISTANCE 3
● ULTRASONIC TRANSMITTER / RECEIVER
■ RADIOFREQUENCY TRANSMITTER / RECEIVER

Figure 3.

System Hardware

The USRAD system consists of one surveyor's backpack, fifteen stationary receivers, a master receiver, custom computer interface and counter timer module, Compaq Portable II personal computer, and a small trailer to transport this equipment. The backpack contains the interface circuitry to receive the signal from the field instrument (originally a portable gamma detector), an ultrasonic transmitter and radio frequency equipment to establish a bi-directional communication link with a computer mounted in the trailer. The ultrasonic transmitter is a lead-zirconate-titanate crystal that is in the form of a circular cylinder with a hollow core.

crystal that is in the form of a circular cylinder with a hollow core. The crystal dimensions are 5.6 cm (2.2 in) in diameter and 3.670 cm (1.445 in) in height. This crystalline material and its dimension result in a natural resonating frequency of 19.5 kHz. The crystal is pulsed for 10 msec each second as the data from the portable survey instrument are transmitted to the computer via the radio telemetry link. If the computer detects any problems, either with the data or in determining the surveyor's location, a message is transmitted to the surveyor and displayed on the handheld terminal to alert the surveyor of the malfunction. The backpack can be operated for a normal eight-hour day from a rechargeable gel-cell.

The stationary receivers contain an ultrasonic receiver and a radio transmitter. The dimensions of the metal box that houses the ultrasonic receiver card, transmitter card, and rechargeable gel-cell battery pack are 10 x 10 x 15 cm (3.9 x 3.9 x 5.9 in). Each stationary receiver has a unique radio frequency so that the master receiver can identify which stationary receivers heard an ultrasonic signal. The master receiver therefore contains 15 radio receivers, one for each stationary receiver, and a receiver and transmitter for communication with the backpack. Both the master receiver and the computer are powered by a gasoline-operated generator also carried in the trailer.

System Software

A digitized schematic drawing of the property is stored in the computer prior to the survey using AutoCAD, a commercial computer-assisted drawing software package already widely used at ORNL. The survey data are added to this information. The property schematic is displayed on the computer's monitor. As the surveyor traverses the property, his past and present position are displayed to denote the completeness of coverage by the surveyor. During the survey, the software checks incoming information and alerts the surveyor (via the backpack terminal) if errors are detected either in the survey data or position data. To ensure data integrity, all data are stored on the hard disk every 30 seconds.

The surveyor can view the data in a number of different graphical formats as well as obtain summary reports. The graphical formats supported by the USRADS are Replay, Block Statistics, Contour, and 3-D plots of the radiation data. The Replay program will generate the same display that the surveyor viewed when the survey of the property was completed. The data are replayed in the same order as they were collected. The Block Statistics routine enables the operator to select a grid block size and have the data analyzed for each block. If the mean of the data for a particular grid block is greater than the operator-entered threshold, then that block is highlighted on the CRT, and the statistical information for that grid block are stored in the summary report. Raw data are converted to appropriate units and displayed or printed out in tabular or graphical format. By indicating preset thresholds, areas of contamination can be identified and statistics can be calculated (area size, number of measurements, measurement range, average and standard deviation). Graphical representations are made in two and three-dimensional display. The contour routine generates a summary report and outlines the areas that exceeded the user input threshold. The 3-D plot generates two different views of the data and provides a means by which the surveyor can view the entire data obtained during the survey. Information displayed in the field is output directly into a report-ready format.

COMBINING USRADS AND GEOPHYSICAL INSTRUMENTS

Check for Interference

The first step was to insure that the USRAD system and the geophysical instruments would not interfere with each other. The USRADS backpack contains very little ferrous metal and we found no changes in magnetometer readings taken with and without the backpack. We also found no interference with terrain conductivity (EM31) readings.

Interfacing the Instruments

No change is required in the geophysical instruments or USRADS hardware. Our current efforts are devoted to rewriting the USRAD backpack software to digitize and transmit the terrain conductivity meter's readings. The EM31 is an analogue instrument which can operate in one of two modes: inphase or quadrature. The inphase mode has a non-linear response to conductivity changes but is especially sensitive to sudden changes in near-surface conductivity, as might be produced by a buried drum (6). The quadrature response is directly proportional to the conductivity of an equivalent uniform half-space. This is the mode generally used for geologic mapping and mapping conductive contaminant plumes (7). We are modifying the USRADS software to record both modes simultaneously, along the range switch setting, and to display either data set to the computer operator. We are taking this opportunity to replace the backpack's ROM chips with new chips coded in the C programming language instead of assembler. This will make the backpack software compatible with software written for the COMPAQ portable computer and make the interfacing of USRADS with other survey instruments easier by making reprogramming simpler. Work will begin on interfacing a magnetometer with USRADS at the same time as the terrain conductivity/USRAD system is being field tested.

Field Testing

We expect to begin field testing in August, 1988. There are several locations on the Oak Ridge reservation where terrain conductivity and magnetometer surveys have been conducted on a grid surveyed by transit. We plan to re-survey one or more of these areas and compare the time required to complete the geophysical surveys and the quality of the results with those of the earlier surveys.

SUMMARY AND CONCLUSIONS

Geophysical surveys are frequently a part of initial investigations at hazardous waste sites. Searching for buried drums with a magnetometer is a classic example. The slowest step in a geophysical survey consists of locating the measurement points, and often this step has to be repeated when the geophysical data suggest that the survey grid needs to be expanded or refined. By combining the USRAD system with geophysical instruments this step can be virtually eliminated as the surveyor's position and the instrument's reading are automatically recorded every second. Only a few ultrasonic receivers have to be located in advance. In addition, the computer operator can notify the surveyor when the data displayed on the portable computer suggests that an anomaly has been found, and additional measurements are needed. Thus the USRAD system will add automatic position location, real-time data processing, and automatic data transcription to geophysical surveys.

ACKNOWLEDGEMENTS

This work was performed by Oak Ridge National Laboratory operated by Martin Marietta Energy Systems for the U.S. Department of Energy under contract DE-AC05-84OR21400.

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DISCUSSION

WAYNE SAUNDERS: What are the costs to develop this system? I don't know what the frequency is of the transponders, to find yourself at a certain location. Did that have any interference with the EM31, either the quadrature or the in phase?

JONATHAN NYQUIST: We didn't find any interference with the radio frequency in the EM31. I think it will cost something on the order of $10,000.00 to $15,000.00.

WAYNE SAUNDERS: What does the unit weigh, the back pack?

JONATHAN NYQUIST: It weighs about 18 pounds.

HARRY McCARTY: Given that the back pack weighs only 18 pounds, did you ever consider using Loran-C or something like that for positioning, especially if you're going to a multi-acre site, and you don't want to have to set up transponders? Did anything get done on that at all?

JONATHAN NYQUIST: We have thought about using some kind of little position syntax to locate the first couple of points, on your grid on the big map, before the small areas are surveyed. I think you could do that. We haven't added it in, because the whole thing starts getting costly.

ROY JONES: Is this system affected by industrial power distribution systems, transmission lines, things like that? Do you have anomaly problems?

JONATHAN NYQUIST: I don't know if it's been tested right next to a transmission line, but the system was originally developed to work in back yards in surveying properties. It's not really affected by being near telephone lines, power lines, houses, buildings, that kind of thing. That's one of the reasons they went to ultrasonics for the locating, rather than a radio locating system.

ALDO MAZZELLA: It looks like your transponder locates yourself in terms of X,Y coordinates horizontally. Many geophysical techniques also need topographic directions. How do you incorporate that into your system?

JONATHAN NYQUIST: The way they have been thinking about trying to do that is by putting a second ultrasonic transmitter above the first and using the phase difference from each of those pulses to their stationary receivers to pick up the altitude. That is a major redesign. It is not a simple thing to add in, and it is going to depend on somebody willing to fund that.

ALDO MAZZELLA: On the magnetometer, did you correct for the cleanness of your system?

JONATHAN NYQUIST: Yes, we did look to see if there was any interference from the backpack itself. It's almost all aluminum components, so there really wasn't anything the magnetometer saw. When we measure with and without the system being operational, we didn't see any difference.

PROTOTYPE VOLATILE ORGANIC COMPOUND (VOC) MONITOR

Joseph D. Wander
Environmental Sciences Branch
Environics Division, Headquarters
Air Force Engineering and Services
Center, Tyndall AFB FL

Barbara L. Lentz
Larry Michalec
Victoria Taylor
S-CUBED Corporation
La Jolla CA

ABSTRACT

The Air Force is sponsoring development of a prototype "smart" instrument package, centered around purge and trap concentration and gas chromatography, to monitor concentrations of VOCs in water. This system will provide timely analytical support for efforts to characterize and remediate VOC-contaminated sites on Air Force bases.

INTRODUCTION

During the past 40 years, Air Force (AF) aircraft operations and engine maintenance have involved enormous quantities of organic liquids, the constituents of which are subject to regulation as volatile organic compounds (VOCs). In 1981, the AF initiated the Installation Restoration Program (1) (IRP), which is a systematic effort to identify and repair sites where soil and water contamination have resulted from mission-related activities.

IRP action at a contaminated site follows a four-step sequence:

(1) identify the problem,
(2) characterize its magnitude and its distribution,
(3) select or develop proper remedial technology, if needed, and
(4) issue contracts for the remediation effort.

Water analyses from monitoring wells are used during the site characterization process and in evaluating the progress of the remediation. If pump and treat methods are selected for remediation, effluent water must also be certified for discharge.

The VOC monitor was conceived to support efforts under IRP by providing rapid, reliable, onsite analyses of VOCs in water samples.

INITIAL CONSIDERATIONS

The development of the prototype VOC monitor was separated into two phases. The objective of phase 1 was to design and field test a system able to perform automated analyses of a single VOC. The objective of phase 2, which was to follow an evaluation of the initial prototype, is to design, build and field test an enhanced prototype, able to perform concurrent analyses of 10 VOCs in a water sample.

Four requirements were imposed upon designs for all phases during development of the VOC monitor:

(1) speed of analysis -- offsite sources for water analyses require an inconveniently long turnaround time of several days to several weeks;
(2) simplicity of operation -- site personnel are presumed to have little or no chemical training;
(3) internal control of reliability -- site personnel are presumed to have limited capability to judge quality of data; and
(4) ruggedness -- resources for onsite repair and maintenance are limited.

PHASE 1 PROTOTYPE

Proven, off-the-shelf purge and trap and gas chromatography units were selected as the analytical hardware for the phase 1 prototype; a 10-position autosampler was included to allow unattended operation. Factors in the selection of the specific hardware components included the fact that all three units are serviced by the same manufacturer's customer support organization, and a reasonable expectation that the components would remain available for several years.

Chromatography was performed on a 6-ft x 1/8 in stainless steel column packed with 1 percent SP-1000^{TM} on 60/80 mesh Carbopack B^{TM}, in close correspondence with EPA Method 601; however, a flame ionization detector (FID) was selected for sturdiness and simplicity. Owing to the possibility that halogen-induced suppression of ion formation would render the FID too insensitive for this application, trichloroethylene (TCE), which was the object of an ongoing IRP effort at an AF location in Michigan, was chosen as the analyte for the phase 1 prototype. This selection provided both a worst-case test for the concept and a practical situation in which performance of the monitor could be evaluated.

An external jack from the FID output was connected to an analogue-to-digital converter (A/D) and thence to a personal computer (PC). Instrument operation, data acquisition, data processing, reporting of the results of the analyses, quality assurance, and assessment of deviations from control or failure to detect internal standard signals are managed by resident software, which is activated at the start of the analysis by a single, menu-directed keystroke.

SAMPLE PREPARATION

The analytical procedure is detailed in an operator's manual (2) that accompanies the phase 1 monitor. Water samples (collected according to EPA-specified procedures) are delivered carefully into an inverted 25-mL syringe. After replacement of the plunger, the syringe is gently inverted. Air and excess water are expelled until 5.0 mL of water remains in the syringe.

The tip of a 50-µL syringe is inserted through the tip of the large syringe into the water sample, to deliver a 10.0-µL aliquot of a solution containing 5.0 ng/µL each of three internal standards: bromochloromethane (IS1), 2-bromo-1-chloropropane (IS2) and 1,4-dichlorobutane (IS3). The sample is delivered at once into the purge vessel, where it is secure until analyzed.

PHASE 1 SOFTWARE (3)

Output from the FID is sampled at 1 Hz; the signal from the A/D is 12 bits, which allows a maximum integer value of 4095. Data from the A/D are stored in an integer array in RAM during the chromatographic run. At the conclusion of data acquisition, the array is smoothed with a five-point least-squares procedure (4) prior to application of a peak-detection routine based on a three-point, forward-looking window (5).

The peak detection routine uses a "four-point rising tangent" criterion to locate the start and end of each peak, plus a first-derivative test to assure detection of sharp peaks. A confirmatory test (5) based on the second derivative is applied to eliminate false identifications. Peaks so located are stored in an "uncorrected" data array as sets of four parameters: peak start point (S_i), peak end point (E_i), peak maximum point (M_i) and uncorrected peak area (U_i).

A baseline correction (5) routine is then applied to the smoothed integer array, which calculates a "chromatographic baseline" by fitting a series of line segments between maximally separated values of S_i and E_i chosen such that no point S_i or E_i falls beneath any baseline segment. For each of the peaks detected, the area (C_i) beneath the chromatographic baseline between S_i and E_i is determined and entered into a "correction" matrix. The final "corrected" data array describing the true peak areas ($[A_i]$) is generated by subtraction of $[C_i]$ from $[U_i]$.

ASSIGNMENT OF INTERNAL STANDARD PEAKS

The software searches for peaks in a window from 0.5 x $t_{2,std}$ (a stored value for the retention time of IS2) to 1.5 x $t_{2,std}$. For each of the peaks encountered in this window at actual retention time $t_{2,p}$, proportional retention times ($t_{1,p}$ and $t_{3,p}$, respectively) are calculated for IS1 and IS3. These three values are inserted into the following function from multivariate statistics (6):

$$\cos \Theta_t = \frac{\sum_{i=1}^{3} t_{i,std} \times t_{i,p}}{\left\{\sum_{i=1}^{3} t_{i,std}^2 \sum_{i=1}^{3} t_{i,p}^2\right\}^{1/2}}$$

The corresponding areas ($A_{i,p}$) of the three peaks under scrutiny are inserted into a similar calculation of $\cos \Theta_a$, for which standard areas ($A_{i,std}$) are stored at the same time as $t_{i,std}$.

Finally, a six-dimensional parameter is calculated for this set of peaks:

$$\cos \Theta = \cos \Theta_t \times \cos \Theta_a$$

The next set of peaks is examined in the same way, and the set giving the larger value of $\cos \Theta$ is stored for the next comparison until all such sets have been examined. If all three IS peaks are located and $\cos \Theta \geq 0.7$, the retention time of the analyte (TCE) is calculated by direct proportion, and the TCE peak is identified as the peak nearest the calculated position (within ± 3 percent of the value calculated). Finally, the peak area is converted into a concentration, which is reported by the printer.

CALIBRATION

Every 10 days, or whenever the QA manager finds the system to be out of control, the operator is required by the software to perform a calibration. A water sample and three prepared standards, at TCE concentrations of 1.5, 4.0, and 10.0 ng/mL, are analyzed. The software performs a series of three linear least squares fits of the three concentrations of TCE to the ratio of the corrected areas of the analyte peaks to the corrected areas of the peaks corresponding respectively to IS1, IS2 and IS3. If $\underline{r} \geq 0.9$ for each of the three fits, the unit accepts the calibration and analytical operation may be resumed; if not, the unit will perform no analyses until the fault is corrected and a satisfactory calibration is performed.

CALCULATION OF CONCENTRATIONS

The value A_i from the corrected data matrix corresponding to the retention time M_i assigned to the analyte is divided in turn by each of the areas of the internal standard peaks, and the quotients are substituted into the respective linear expressions defined during the calibration procedure.

The result is three values of the concentration of the analyte in the same units in which the calibration was performed. The software then computes the mean ($\bar{x}$) and standard deviation ($\underline{s}$) for the three values. If any of the values differs from $\bar{x}$ by more than $2\underline{s}$, it is declared an outlier and rejected. The concentration is reported as the mean of all values not rejected.

THE REPORT

Data reported for all peaks detected are the retention time and A_i. If no error flags were set, the concentration of the calibrated analyte is printed; otherwise, the message(s) defined by the flags are printed. This format is intended to let the printed output serve as a complete documentation of the analytical result and the control status of the analytical method, which will satisfy requirements of environmental regulatory agencies. The results, date, time and operator are stored in compressed form in an archival file for verification.

QUALITY ASSURANCE

Two QA procedures were incorporated in the phase 1 prototype. The Procedural Guide (2) specifies that a standard (now 4.0 ng/mL) be analyzed daily at the conclusion of a series of samples to verify that the calibration has not failed. If the value reported differs by more than $2\underline{s}$ from the mean of the control chart for the daily determinations, the operator is instructed to conclude that the system is out of control and to perform a recalibration.

The software also calls for spike and duplicate spike analyses of every tenth sample. A 5-μL aliquot of a methanolic solution containing 10 ng/μL TCE is added to two duplicate samples, which are then analyzed "normally." The results of the two spiked samples are compared with the result of the unspiked analysis, and with each other. If the mean recovery of TCE from the two spiked samples is less than 75 percent or more than 125 percent, a flag is set to print a report that accuracy criteria are not satisfied and to require recalibration. If the difference between results for the pair of spiked samples exceeds 25 percent of the amount of the spike, a flag is set to report that reproducibility criteria were not met and to require recalibration.

PHASE 1 FIELD EVALUATION

In September 1986, The phase 1 prototype was installed in the field, at the the sewage plant serving Wurtsmith AFB. Some minor renovation was required during installation to provide bench space and isolated electrical service. The only standard laboratory facilities available were a fume hood and a balance.

In this environment, the system has performed satisfactorily throughout the evaluation. The first data set generated for a split-sample evaluation was submitted to, and accepted by, EPA Region V as support for an application for local alternate test procedure (ATP) status for the system and method. Approval as a local ATP was given in February 1988.

OBSERVATIONS

Three spontaneous mechanical failures occurred during the test period, which ended in November 1987. All three (failed heater connections [two times] and dirty contacts on a printed circuit board in the gas chromatograph [Varian 3400] plus misalignment of a six-port valve inside the Tekmar purge and trap unit) required intervention by project personnel. A subsequent incident, also involving valving in the purge and trap unit, was managed successfully by site personnel, with help from Varian's customer support organization (provided under a continuing annual service contract, which has been in effect since the installation).

Effective orientation and education of site personnel was the most-difficult task in the phase 1 effort, and experience gained during this part of phase 1 has directed a number of changes in the way in which the phase 2 software will interact with the operator. Documents accompanying the phase 2 monitor will be expanded to include suggestions about inventory requirements and AF sources for supplies, and to recommend security measures to protect the monitor from incidental damage.

A presumably site-specific problem (under investigation) that emerged was a chronic (estimated to be of the order of 50 parts per trillion) background interference from a VOC not positively identified but isographic with benzene. The phase 1 unit successfully discriminated against the interferent when TCE was present at levels above its threshold for detection (about 0.5 parts per billion), but it routinely identified the interferent as TCE when the actual TCE peak was below the detection threshold. (Because the other VOCs in the list below have either a higher action level or more sensitivity at the FID, this is not expected to be a problem to the phase 2 prototype.)

PHASE 2

Current models of the same components were procured for assembly into the phase 2 prototype, which was to be an improved version of phase 1, able to perform concurrent analyses (in individual water samples) of as many as 10 VOCs from the following list:

benzene	
chloroform	
dichlorobenzenes	(DCBs)
1,1-dichloroethane	(1,1-DCA)
1,1-dichloroethylene	(1,1-DCE)
cis-1,2-dichloroethylene	}(1,2-DCE)
trans-1,2-dichloroethylene	
ethylbenzene	
methylene chloride	
1,1,2,2-tetrachloroethane	(1,1,2,2-TCA)
tetrachloroethylene	(PCE)
toluene	
1,1,1-trichloroethane	(1,1,1-TCA)
trichloroethylene	(TCE)
xylenes	

A different PC (compatible with the phase 1 software) was selected when the original unit went off the market. A chip was added to support floating-point calculations. After assembly of the hardware for the second prototype, it was established that the combination of chromatographic resolution and data sampling rate was inadequate to provide reliable separation of and discrimination between 1,1,2,2-TCA, PCE and IS3.

Rather than abandon the commercially available and accepted internal standards, we increased the data sampling rate (7) to 9.11 Hz. This improved the reliability of peak discrimination by the software, but it also established that the chromatographic separation was insufficient. Accordingly, we replaced the packed column with a 30-m x 0.53-mm fused silica capillary column coated with DB-624^{TM}.

The increased data-sampling rate also created new problems in dealing with the baseline, requiring reoptimization of baseline-correction and peak-detection algorithms, which were written for a 1-Hz data rate.

The promulgation of 40 CFR 141 created a requirement that vinyl chloride be measured whenever two-carbon halogenated species are detected in waters to be used for drinking. Accordingly, vinyl chloride was added to the list above to preserve the option of discharging a treated stream into a potable water supply.

Methanol, the accepted solvent for VOC standards, is incompletely separated on the DB-624^{TM} column and obscures vinyl chloride at the FID. As EPA discourages the use of aqueous calibration standards, we invoked a hardware method to remove methanol.

Nafion^{TM} membranes are widely used in devices to remove water from gas streams (8-11). Loss of polar organics has been documented in gas streams so treated (9), and methanol is reported (10) to cause reversible swelling of these membranes. Baker (11) reported >90% removal of methanol from a compressed gas stream passed through a long-path Nafion^{TM} dryer.

Based on these separate reports that methanol diffuses through Nafion^{TM} and that VOCs are transmitted efficiently through such driers, we opened the stainless steel transfer line between the sparger and the trap and used Swagelok^{TM} connectors to insert a 12-in section of 1/16-in Nafion^{TM} tubing. The tubing is temporarily enclosed in a 1-in dia x 2-in plastic tube that is partially filled with calcium sulfate and purged with dry nitrogen to sweep out solvents as they diffuse through the membrane. Preliminary evaluation of this separator showed efficient removal of methanol.

The loss in simplicity of design and in ruggedness of the column is compensated by several gains:

(1) the baseline rise during temperature programming of the packed columns ceases to be a problem;

(2) the VOCs are completely separated;
(3) the interference with detection of vinyl chloride is eliminated;
(4) the chromatographic method is in correspondence with more-current EPA methods (524 and 624).

Other changes from phase 1 will include decreasing to three days the maximum period between recalibrations for analytes, replacing the Tekmar ALS-10 with a true autosampling device that will accept 40-mL collection bottles and introduce internal standards during injection, interactive assistance to the operator in performing the analysis and in troubleshooting, and an interactive orientation and training program to facilitate acceptance of the monitor by new operator-trainees.

STATUS OF PHASE 2 PROGRAM

After the bugs have been worked out of the software and specific procedures have been defined for calibration and analysis, the phase 2 prototype will be installed at a base in California for onsite evaluation. The target date for the installation is January 1989, and a six-month evaluation period is planned.

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DISCUSSION

JOSEPH ROESLER: On volatile organics, the official EPA method for sampling is a manual method. That's the only way you're allowed to sample volatile organics. And it's written up in their procedures. Therefore, if you use an instrument to sample volatile organics, you must have an alternate test procedure to use the other technique.

JACOB GIBS: There are a number of commercially available chromatographic software packages that do approximately 80% of what you've talked about here. What would have been the difference to you of one of asking those vendors to modify the program for the other 20% that you needed to make it "idiot proof," as opposed to doing everything on a clean sheet of paper?

JOSEPH WANDER: The packages didn't exist when we started (this goes back to 1983). There is some lag time. I had considered going to a soil gas device, using this same system, and I have been going through exactly the same question. I'm not sure we can do it economically for what they can.

ENVIRONMENTAL FIELD SAMPLING EXPERT SYSTEM
DEVELOPMENT OF A SOIL SAMPLING ADVISOR

R. A. Olivero, R. E. Cameron, K. J. Cabble
M. T. Homsher, M. A. Stapanian
Lockheed Engineering & Sciences Company
1050 E. Flamingo Rd., Las Vegas, NV 89119

K. W. Brown
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
P.O. Box 93478, Las Vegas, NV 89193-3478

ABSTRACT

The generation of data of known and acceptable quality for environmental decision-making requires the use of sound technology at every step of the measurement process. The field sampling step can introduce an uncontrolled amount of uncertainty in the data. This variability might be enough to compromise the attainment of the overall data quality objectives of the project in spite of efforts to optimize instrument performance and analytical method reliability. Computerized tutorials and decision support aids, such as expert systems, can assist in the planning of environmental field sampling projects by providing to planners a sound body of knowledge about sampling. This paper describes the development of a pilot expert system that assists the sampling manager in evaluating alternative procedures in view of project data quality objectives and hazardous site characteristics. The increased access to a more scientific and systematic methodology for planning a sampling project will result in significant benefits: reduced variability due to sampling errors and deficiencies, reduced potential for sample contamination, increased representativeness, more efficient use of the usually limited sampling resources, and an appropriate match of allowed error and required data quality to provide the information needed for decision making. The present stage of the system development addresses soil sampling for inorganic target analytes, which are included in the Contract Laboratory Program, as a test subset of the complexities of the sampling problem.

Key words: Environmental sampling, soil sampling, expert systems, data quality objectives.

INTRODUCTION

The generation of analytical data of appropriate quality for monitoring, cleanup, and exposure assessment projects requires a combination of capable instrumentation, sound methodology, and representative sampling. Appropriate data quality is determined at the outset of a project when data quality objectives (DQOs) are defined. The subsequent stages of sampling, chemical analysis, data review, and data interpretation need to be planned in accordance with the identified data quality needs. The U.S. Environmental Protection Agency (EPA) has issued guidelines and procedures for generation of data used in environmental decision making [1, 2].

Sampling and analysis can be major sources of uncertainty in the data if appropriate quality assurance and quality control (QA/QC) measures are not implemented. An effective data quality review subsequent to data collection and analyses can unveil deficiencies in data quality but cannot prevent the deficiencies. There is no substitute for conscientious planning of hazardous site monitoring activities to ensure a rational use of resources and the attainment of the stated DQOs.

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Traditionally, development and improvement of instrumentation for chemical analyses and analysis protocols have received more attention than sampling procedures and their related QA/QC aspects. Considerable improvement has been made to laboratory and field instrumentation and methodology in the areas of precision, bias, and sensitivity. However, sampling variability is still a difficult-to-control source of uncertainty in the measurement process. The use of deficient sampling procedures has a severe, adverse impact on the usefulness of the data. The improved analytical performances available today should be considered in the proper perspective as only one component of the overall performance of the measurement process.

Sampling plans need to be specific as to the objectives of the study and the hazardous site characteristics. This need makes the standardization of sampling procedures and protocols a difficult task, and it may result in the use of inappropriate or oversimplified sampling practices. In such a case the generation and use of environmental data may be based on sampling procedures of unknown quality. In particular, personnel involved in the development of sampling plans for environmental field monitoring may face difficulties resulting from the lack of sufficient standardized procedures, rapidly changing technology, scarcity of experts, lack of knowledge, insufficient training, and inadequate information.

The development of a sound sampling plan involves a large number of decision points and requires expertise and experience derived from several disciplines such as environmental engineering, chemistry, geology, soil science, statistics, management, and field operations. A sampling expert must have the ability to combine all the aspects of the disciplines involved, as well as field experience and related formal training. Written manuals do not always adequately provide the nature and amount of background and expertise required for the appropriate planning of a sampling project.

To compensate for deficiencies in personnel background and experience and the inadequacies of written manuals, computerized decision support aids and tutorials are an alternative for providing assistance in the planning of environmental field sampling projects [3]. This type of system can make available to the planning team a sound body of knowledge compiled from leading experts in the subject, and other recognized sources, and provide for structured presentation in a format that delineates a natural decision pathway.

EXPERT SYSTEM FOR ENVIRONMENTAL SAMPLING

A computerized system to assist personnel in planning a sampling project, to evaluate the relevant factors for the specific hazardous site assessment, to identify data quality objectives, and to select the appropriate features for the sampling plan, is currently under development. The system makes specific recommendations regarding appropriate sampling procedures within the limitations of its current knowledge domain. These recommendations are based on information elicited from the user through consultations with the computer. The goal is to assist the user in devising a sampling plan that will attain the project DQOs with appropriate technical, statistical, economic, procedural, and safety considerations.

This computer program falls within the category of expert systems [4]. Expert systems can be defined, in general, as computer programs that incorporate the knowledge of, and simulate the decision-making processes of, human experts in order to achieve a high-level of performance for a particular task. Expert systems contain a body of knowledge in the form of facts and decision rules (a knowledge base) and a mechanism for attaining logical conclusions from that knowledge (an inference engine). The system is able to query the user for relevant information, and recommend appropriate solutions, based on the stored knowledge base.

Preliminary studies revealed that the enormous scope of the overall sampling problem for a Superfund study hampers the probability of success of any attempt to develop a comprehensive initial expert system. There is a broad range of tasks (e.g., DQO determination, methodology selection, and safety considerations), analytes (e.g., volatiles, semivolatiles, pesticides, inorganics, and radioactive materials), and matrices (e.g., air, water, soil, and biota) involved. All of these variables must be considered to define and undertake a sampling plan [5].

This paper describes a pilot expert system that is being developed to provide "intelligent" assistance in the various aspects of soil sampling, with emphasis on determining the inorganic target analytes included in the EPA Contract Laboratory Program (CLP). Soil was chosen because environmental assessments involve soil sampling on a frequent basis and, compared to aqueous or aerial systems, soil is a relatively static medium. The need to deal in this first expert system with the complications associated with more active transport phenomena has thereby been avoided.

The expert system prototype addresses the issues involved in sampling for inorganic target analytes, an area for which procedures are commonly accepted. A real need for guidance, expertise availability, and common acceptance of the proposed recommendations are key elements for the feasibility of developing a successful expert system.

CONCEPTUALIZING THE SAMPLING DESIGN

Sampling issues, as well as analysis issues, must be addressed early during the process of determining the DQOs. This is to ensure that the selected sampling scheme is in accordance with DQO requirements. The main characteristics defining a given sampling process are precision, accuracy, and representativeness and their contribution to the total error acceptable in the decision. The details of the sampling procedure should be designed to achieve the levels of these parameters defined by the project DQOs [6].

Both user factors and site factors determine the design of the sampling plan. Figure 1 depicts the interdependencies among the several factors involved. Analytes of interest, intended use of the data, and resources available are summarized in the statement of the DQOs, which in turn determine the analytical method requirements. The source, type, and extent of contamination, as well as field conditions, complement the input for preparation of a sampling plan. Based on information about these aspects, the expert system provides advice on a number of categories that form part of the sampling plan. These categories are: requirements for attainment of statistical confidence and representativeness (e.g., sample size, number, and location); quality assurance and quality control (QA/QC) measures; sampling procedures, techniques, and equipment; sample handling and shipping; documentary procedures; archiving and retrieval; resource requirements; and safety measures [7].

SCOPE OF THE SOIL SAMPLING EXPERT SYSTEM PROTOTYPE FOR METAL CONTAMINANTS

The domain of applicability of the expert system prototype was constrained in order to allow a clear identification of sampling situations that it is intended to address, and those situations that fall outside of its capabilities.

The contaminants addressed are the EPA CLP inorganic target analytes. Cyanide is included in this list together with the metal contaminants. The type of contamination source considered is surface-level or fallout (e.g., from stack emissions). CLP inorganic target analytes in soil have variable migration and solubility rates, although the majority of the analytes may have a slow migration rate unless a transport medium is active. For the purpose of this prototype, sampling is performed close to the surface for surface-level contamination sources. Also for prototype and sampling purposes the site is assumed to be a flat, rectangular area, with uncomplicated site and medium characteristics. Several zones with different contamination levels or distributions can be managed.

The driving factor for the expert system is the statement of the data quality objectives for the project. The EPA-defined DQO process requires definition of the decision to be made and

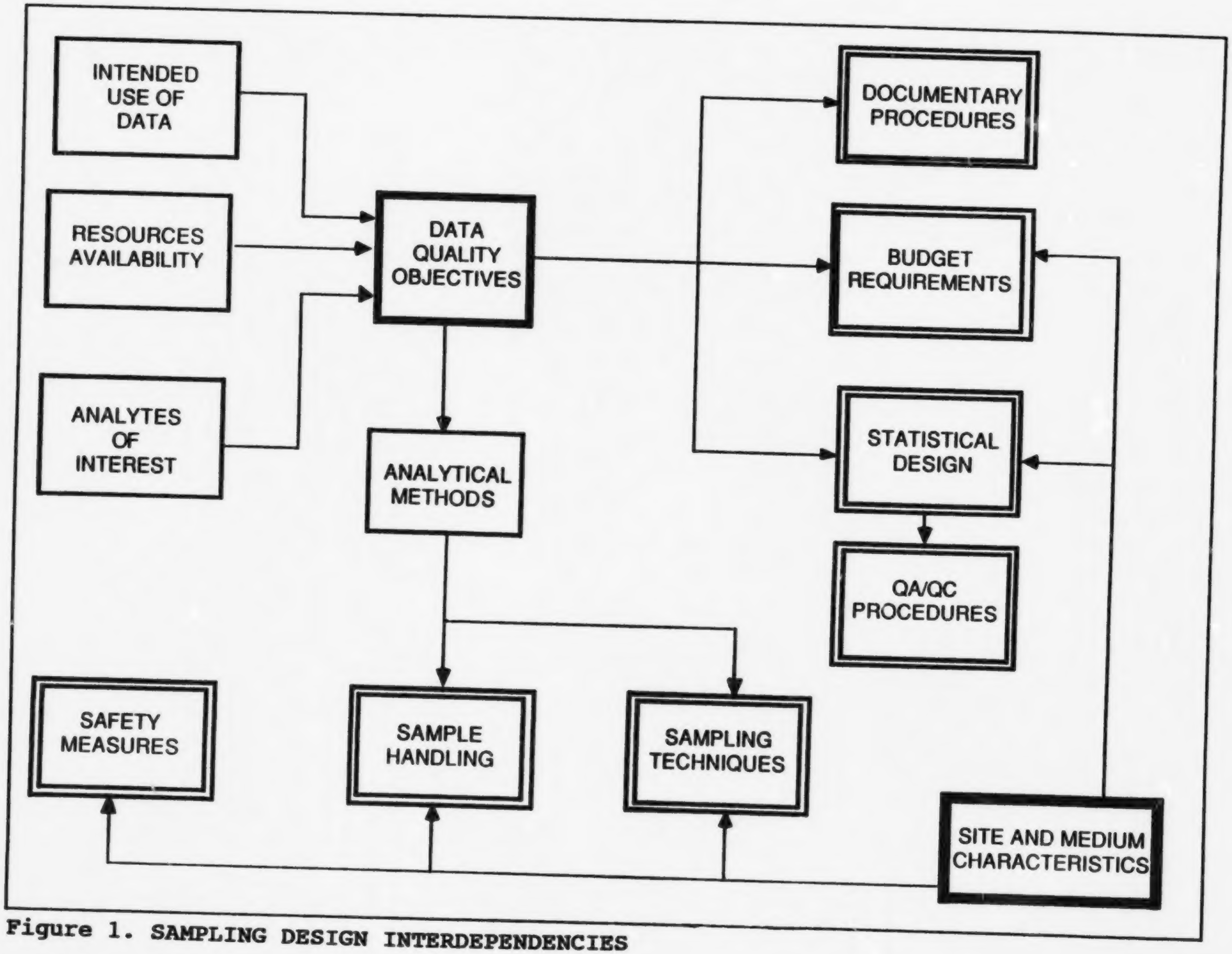

INTENDED USE OF DATA
RESOURCES AVAILABILITY
ANALYTES OF INTEREST
DATA QUALITY OBJECTIVES
ANALYTICAL METHODS
DOCUMENTARY PROCEDURES
BUDGET REQUIREMENTS
STATISTICAL DESIGN
QA/QC PROCEDURES
SAFETY MEASURES
SAMPLE HANDLING
SAMPLING TECHNIQUES
SITE AND MEDIUM CHARACTERISTICS

Figure 1. SAMPLING DESIGN INTERDEPENDENCIES

the data needed to support the decision; these identifications are made in Stages I and II of the process. The expert system assumes that these stages have been completed and then proceeds to gather summary information about the quantitative aspects of the decision. Some aspects are a description of the the data to be collected, the domain (spatial and temporal) for the decision, the statistics to be used to describe the data, and the statement of desired performance in terms of acceptable probabilities associated with false positive and false negative situations. This information is entered into the expert system and used by subsequent modules to help complete Stage III of the DQO process, namely the design of the sampling aspect of the data collection program.

The system makes suggestions concerning the sample analysis technique that is appropriate to meet the data quality objectives. Applicable analysis techniques for EPA CLP inorganic target analytes [8] are inductively coupled plasma-optical emission spectroscopy (ICP-OES) and atomic absorption spectroscopy (with a cold vapor technique for mercury and a colorimetric technique for cyanide) [9]. X-ray fluorescence spectroscopy provides field screening of metal contaminants [10]. The expert system makes recommendations based on the level of data quality required as determined by the DQO module.

The expert system guides the user through a site and medium (soil) characterization process. Information is obtained regarding the physical and ecological nature and configuration of the area and site; animal and vegetation characteristics; surface and groundwater factors; weather and climate data; and identification of manmade structures, activities, and perturbations. The prototype requests information about soil physical and chemical properties which help characterize the "soil contamination system," such as grain size (texture), structure, cohesiveness, moisture contents, color, odor, and various determinations obtained with field monitoring equipment.

The statistical design module finds the minimum number of samples that should be collected for a given set of DQOs. The procedures and underlying assumptions for determining the number of samples and sampling design are outlined in Rogers et al. [11]. The present system uses classical statistical methods. Future designs will also include geostatistical methods to address the experimental objectives. Preliminary data are required for the calculations. The number of samples recommended for statistical analysis depends on the experimental objectives, the accuracy to be achieved, the nature of the pollution source, the expected distribution of the pollutant, and logistical and budgetary constraints [12, 13]. For the prototype system, four objectives have been identified: (1) finding the average pollutant concentration at the site, (2) finding the spatial variability of the pollutants at the site (e.g., identifying "hot spots"), (3) comparing the pollutant concentrations of different subareas of the site, and (4) finding the temporal variability of the pollutants at the site. The accuracy to be achieved is related to two types of errors that can occur in decision making, namely false negative and false positive determinations. The nature of the contamination source (point or nonpoint) and distribution of the contaminant (homogenecity and continuity) are also taken into account for the design. The system accommodates the condition where concentrations may vary in subareas, or strata, at the site due to differences in soil type, topography, or other physical characteristics. Samples may be taken at points in a rectangular grid or at random coordinates at the site. The system produces a listing of the local coordinates where the samples are to be taken.

The system provides recommendations for a rigid QA/QC program to statistically evaluate the quality of the data at each step of the analytical process and to make sure that the quality of the data is adequate for the purposes for which the data will be used [14, 15]. The objectives of the QA/QC procedures are to measure and obtain (1) accuracy, (2) comparability, (3) precision, and (4) representativeness of the data. These characteristics are measured and monitored by collecting and analyzing the appropriate number of blanks, standards, and duplicates along with the actual environmental samples.

Recommendations are provided for the appropriate sampling tools and equipment and method of sampling. Depending on the depth of the contaminants and soil characteristics, various types of equipment may be recommended, such as a trowel, scoop, auger, drive tube, and split spoon [5,16,17,18]. The system also makes suggestions on the equipment material and decontamination procedures.

Depending on the contaminants under consideration and the analytical technique to be employed, the expert system provides advice on the appropriate sample handling techniques [19] (i.e., sample manipulation, container type, preservation, shipping, and holding times).

The user is also queried on expected and potential personnel hazards on the site. The expert system then classifies the situation accordingly, and provides details on the required level of personal protection as well as general safety measures and equipment needed [20, 21].

The system can supply information on standard documentation and chain-of-custody procedures. These include sample identification, logbooks and records for samples, instrument calibration, QA/QC, and chain-of-custody records [18]. The rationale behind each documentary procedure is explained to the user, and lists are given with the required items of information for each form.

The primary consideration in budgetary requirements is to meet the user's needs according to the DQOs. Secondary considerations include, but are not limited to, safety procedures, site conditions, climate and weather conditions, and sampling techniques. In response to input about cost elements for sampling (e.g., travel, salary, rentals, etc.), the number of samples (including QA/QC samples) provided by other modules, and sampling throughput estimates, the expert system provides estimates for required dollars, personnel, and time for sampling.

SYSTEM DESIGN AND DEVELOPMENT

Most currently available computer programs that can be used in conjunction with sampling fall into the category of data analysis aids. Many are used after the data have been gathered and thus flaws are discovered after the fact and are costly to correct. Planning tools that offer simulation based on statistical techniques handle numerical data only. Blind automation of simulation, or analysis processes, introduces the risk of lending creditability to conclusions that have been reached by applying the wrong procedures.

The expert system described in this paper handles both hard data (i.e., facts and performance numbers) and soft data (e.g., judgments, risks, projections, intuition, and human factors). Mathematical capabilities to handle statistical aspects of the problem are combined with symbolic reasoning to make rule-based decisions on what sampling procedures to use. Table I is an example of simple inference rules.

Expert system techniques are used to infer the appropriate procedures to be used in each sampling situation. The expert system contains knowledge in the form of rules that will allow it to search for appropriate recommendations based on facts about the sampling problem elicited from the user (Figure 2). The knowledge entered into the expert system knowledge base has been drawn from EPA-published manuals and other Federal agency (USDOE and USDA) and reports, peer reviewed literature, and from interviews with environmental scientists experienced in soil sampling. This knowledge, based on experience in both field and laboratory, is mostly in the form of "rules of thumb" for decision making in the planning of sampling projects, of numerical formulas, and of procedures for statistical calculations.

The IBM-PC-compatible microcomputer was used as both development and delivery environments because it provides availability and portability advantages. The computer program is written within an expert system development shell. The selected software package is KnowledgePro (Knowledge Garden, Inc., Nassau, New York), a knowledge-processing software package that combines expert system and hypertext capabilities [22]. Hypertext [23] is a method of presenting computerized knowledge. Preselected words and phrases on the computer screen can be highlighted and additional explanations requested about them. Figure 3 gives an example of

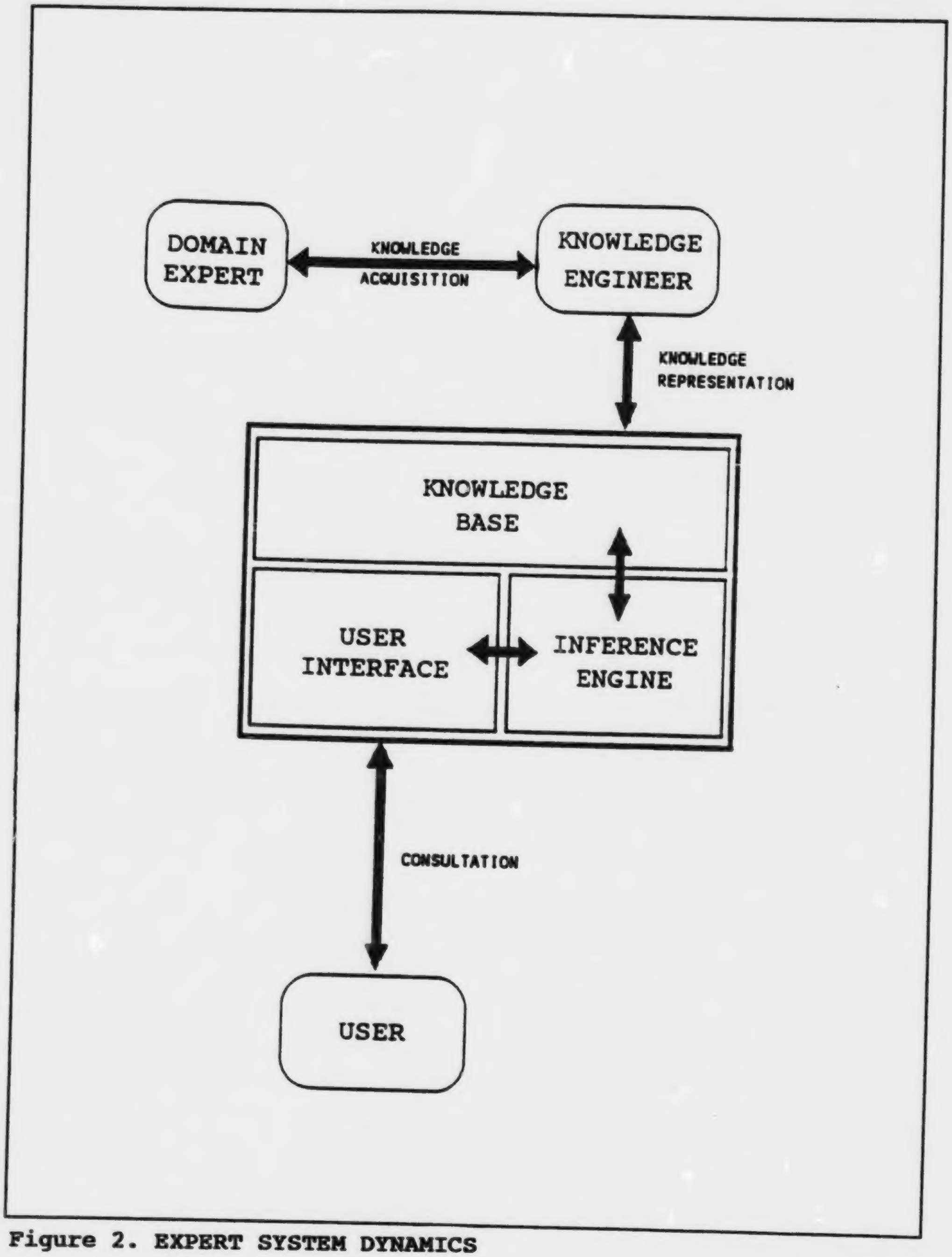
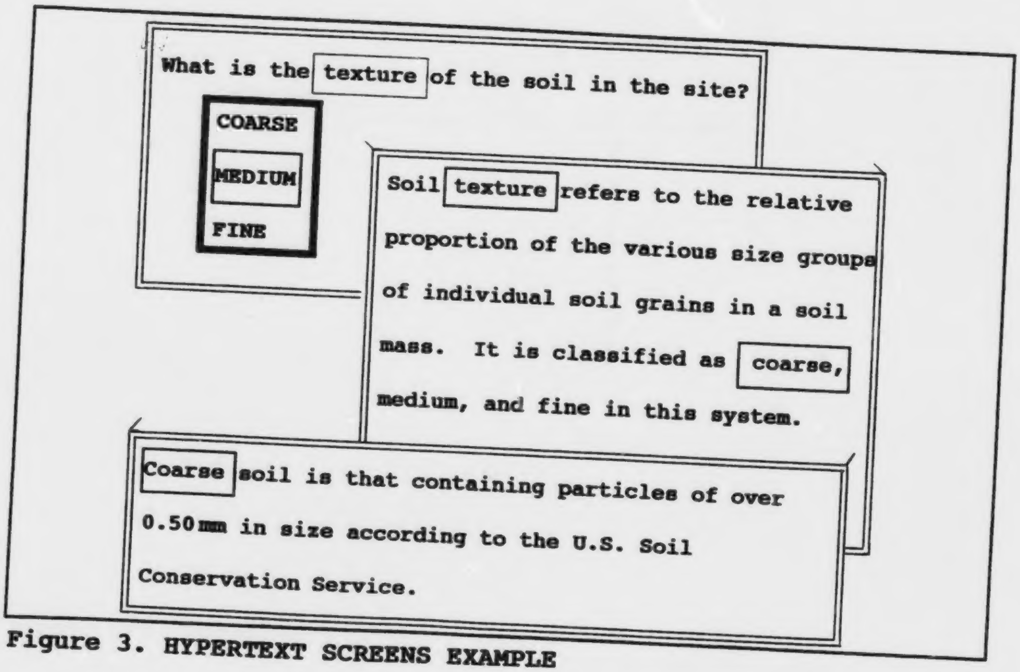

DOMAIN EXPERT
KNOWLEDGE ACQUISITION
KNOWLEDGE ENGINEER
KNOWLEDGE REPRESENTATION
KNOWLEDGE BASE
USER INTERFACE
INFERENCE ENGINE
CONSULTATION
USER

Figure 2. EXPERT SYSTEM DYNAMICS

IF	SAMPLING DEPTH	IS MORE THAN 0.6 METERS
AND	SAMPLING DEPTH	IS LESS THAN OR EQUAL TO 4.9 METERS
AND	VERTICAL PROFILE NEEDED	IS POSITIVE
AND	VERTICAL PROFILE TYPE	IS CONTINUOUS
AND	SOIL TEXTURE	IS NOT COARSE
AND	SOIL COMPACTNESS	IS MEDIUM OR FIRM
THEN	SAMPLING TOOL TYPE	IS VEIHMEYER SAMPLER

IF	POLLUTION SOURCE DISTRIBUTION	IS NONPOINT
AND	CONTAMINANT DISTRIBUTION	IS HETEROGENEOUS
AND	HETEROGENICITY TYPE	IS DISCRETE
THEN	SAMPLING DESIGN TYPE	IS STRATIFIED SAMPLING

Table I. EXAMPLE RULES


What is the texture of the soil in the site?

Soil texture refers to the relative proportion of the various size groups of individual soil grains in a soil mass. It is classified as coarse, medium, and fine in this system.

Coarse soil is that containing particles of over 0.50mm in size according to the U.S. Soil Conservation Service.

Figure 3. HYPERTEXT SCREENS EXAMPLE

the use of hypertext technique. This technique allows the user to control the amount and depth of the information that will be presented during the interactive consultation with the computer. This feature is very desirable in a system that is intended for users with a widely varying background or experience in terms of knowledge about planning and conducting sampling projects. This software tool has the capability of combining decision rules for inference with user input to control the system, all within a user-friendly environment. Turbo Pascal routines were interfaced with KnowledgePro to provide a more efficient handling of calculation-intensive tasks (e.g., statistical calculations).

The knowledge was organized in a frame-based structure (see Table II) to allow the application of an object-attribute-value scheme for knowledge representation and reasoning throughout the system. The program structure was modularized to overcome memory and speed limitations.

CURRENT STATUS AND FUTURE DEVELOPMENT

A demonstration prototype for the sampling expert system (soil metals) has been completed and a full prototype is under development. All the modules described in this paper have been implemented and work continues on developing them further. Phased testing and validation are beginning. Testing will include in-house and third party evaluations. The work described is being done under contract to the EPA Environmental Monitoring Systems Laboratory, Exposure Assessment Research Division, Las Vegas, Nevada.

SUMMARY AND CONCLUSIONS

The availability of a decision support and training aid, with appropriate coverage of the issues involved in a sampling plan, including statistics, QA/QC, sampling techniques and procedures, and safety considerations, will provide wide access to more reliable and replicable sampling plan development. This tool should result in the generation of data of acceptable sampling quality, with quantifiable variability possible and bias due to sampling errors and deficiencies; a tracking system for sample contamination; increased representativeness; a more efficient use of the usually limited sampling resources; and a greater reliability in interpretation of results. It enables the researcher to focus on the primary objectives of the study.

The pilot expert system ensures valid data analysis and a quantification of the quality of data at each step, thus conserving expensive sampling and analytical resources while shortening the time for the acquisition of data of known quality to support environmental decisions. The pilot expert system described herein will also serve as a limited training aid for individuals participating in soil surveys of contaminated sites. This type of system allows the user to try "what-if" situations with information regarding site conditions and the desired confidence in the results. The use of the system to plan sampling activities and to validate proposed sampling plans will enable the users to detect potential errors and data deficiencies before they occur, thereby saving time and resources and providing greater reliability for the survey results.

The preliminary experience obtained from the development of this prototype supports the feasibility of a larger and more detailed system. The implementation approach has been tested and found appropriate. Changes can be readily made, and subsequently the expert system could be continuously updated to reflect modifications and advances in environmental sampling.

ACKNOWLEDGMENTS

The authors would like to acknowledge David W. Bottrell (EPA Environmental Monitoring Systems Laboratory, Quality Assurance Research Branch, Las Vegas) for his support of the preliminary studies for the system, Kelly R. York, Lockheed Engineering & Sciences Company (LESC) for

OBJECT/ATTRIBUTE:	SOIL/TEXTURE

VALUE:	COARSE MEDIUM FINE
PROPERTIES:	INPUT FACT
REFERENCE:	SOIL DATA COLLECTION IN SUPPORT OF EMERGENCY RESPONSE ACTIVITIES (PAGES 5-3 - 5-8)

VALUE:	COARSE
DEFINITION:	COARSE SOIL IS CONTAINING PARTICULES OF OVER 0.50 mm IN SIZE ACCORDING TO THE US SOIL CONSERVATION SERVICE
CONDITION:	A COARSE TEXTURE SOIL ACTS AS A CONDUIT FOR WATER AND ANY DISSOLVED CHEMICALS FOUND IN THE WATER. LIQUID CHEMICALS WITH A LOW VISCOSITY WILL OFTEN FLOW THROUGH THE COARSE TEXTURED SOILS

VALUE:	MEDIUM
DEFINITION	MEDIUM SOIL IS SOIL CONTAINING PARTICULES BETWEEN 0.25 - 0.50 mm IN SIZE ACCORDING TO THE US SOIL CONSERVATION SERVICE
CONDITION:	A MEDIUM TEXTURED SOIL WILL INHIBIT CHEMICAL MIGRATION OF LIQUID CHEMICALS WITH LOW VISCOSITY

VALUE:	FINE
DEFINITION:	FINE SOIL IS SOIL CONTAINING PARTICULES LESS THAN 0.25 mm IN SIZE ACCORDING TO THE US SOIL CONSERVATION SERVICE
CONDITIONS:	A FINE SOIL WILL INHIBIT MIGRATION OF MANY LIQUID CHEMICALS

Table II. EXAMPLE FRAME

programming the expert system, and Luis A. Herrera (LESC) for his help during the initial stages of knowledge acquisition.

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APPENDIX - CASE EXAMPLE

This appendix contains a narrative description of a fictitious hazardous site and presents an example of a soil sampling problem for demonstration purposes. This example gives the reader an idea of the type and detail of both input and output information handled by the expert system prototype described in this paper. The recommendations produced by running a consultation session with the Expert System for Soil Sampling Prototype follow the description.

SITE AND PROBLEM NARRATIVE DESCRIPTION

An abandoned storage yard for a battery reprocessing plant in Gray City, Nevada, has been characterized in a preliminary study. Analytical level II quality data on the concentration of lead at the site was gathered on-site with the use of a portable X-ray fluorescence (XRF) instrument. Analyses were performed for other suspected metals, but none were found at any significant concentration.

Stages I and II of the DQO process have been completed. The decision to be made by the state authority is whether or not the site is in compliance with a percentile-based regulation. It has been proposed to determine if a pre-established percent of collected and analyzed samples exceed certain criterion for lead concentration. For this purpose it is necessary to gather data on the concentration of this contaminant in the soil. The required data type is the concentration of lead in the soil in parts per million (ppm). State authorities have established the action level for lead at 1,000 ppm and the percentile testing threshold at 75 percent (it is to be determined if more than 25 percent of the samples have lead concentrations above 1000 ppm or not). The true proportion of samples exceeding the action limit for which the site can be reliably declared as clean is 15 percent. A false negative rate of 10 percent and a larger false positive rate of 20 percent have been established for the determination as tolerance limits.

Contamination is known to have begun at least two years ago. Knowledge about the vertical migration of lead at this site is not available, but the migration rate in similar situations have been determined to be almost negligible. Thus the contaminant should be found no deeper than 6 inches, as confirmed during preliminarily portable XRF measurements.

The site has an area of 5,000 square meters. It is located in an arid area with clear skies and negligible to light winds almost year around. The soil is low in moisture content and texture is medium (particulates between 0.25 mm and 0.50 mm dia.). Soil compactness is medium. The relief at the site is flat and there are no discernible depressions. Portions of the site are covered with grass. Fifty-five-gallon drums marked "SULFURIC ACID" are visible at the southwest corner of the site. Localized high levels of sulfuric acid contamination are suspected as indicated by the distressed affects on the vegetation around the drums and acidic soil pH measurements.

Two areas (strata) of known contamination were identified from the preliminary study by XRF. One is 15 by 26 meters, and the second is 20 by 30 meters in size. From preliminary data, the suspected proportion of contaminated samples greater than 1000 ppm is 90 percent for both areas. Sampling will be confined to these areas.

It is considered that one sampling team of three members is available for this sampling phase. It is estimated that it is feasible to collect and analyze approximately 25 samples per day. The team has determined that a sample loss rate (unanalyzable and uncollectable samples) of 5 % can be expected. The cost components associated with the sampling team operation are as follows:

Travel costs	$ 1500
Supplies costs	$ 500
Service costs	$ 2000
Shipping costs	$ 1500
Average salary per day	$ 125
Per diem rate	$ 80

EXPERT SYSTEM PROTOTYPE RECOMMENDATIONS

The level of analytical quality should be Level III (Non CLP) or Level IV (CLP-quality). An appropriate analytical technique for analysis of lead at this level is graphite-furnace atomic absorption. Historic performance data for the method for lead analysis are:

Precision (% RSD):	9.2%
Accuracy (% BIAS):	-2.2%
Concentration Range:	11.5 - 714 ug/Kg

Grab sampling is recommended. A stratified sampling design is appropriate, with 17 samples for stratum one, and 26 samples taken for stratum two, for a total of 43 samples. This number accounts for the expected sample loss rate due to unanalyzability and uncollectability.

The following QA/QC samples are recommended:

Field blanks	2
Sample bank blanks	1
Reagent blanks	3

Laboratory controls	3
Calibration checks	3
Spiked samples	3
Duplicate samples	3
Total recoverable	2

It is recommended that the site be cleared of vegetation and surface litter before sampling. The appropriate sampling tool is a scoop and/or trowel. The tools should be wrapped in industrial-strength aluminum foil when not in use and cleaned by the USEPA standard decontamination protocol.

On-site sample sieving is not recommended. Sample homogenization is needed. Samples should be stored in 250 mL jars pre-cleaned by the USEPA jar-cleaning protocol C. The recommended maximum sample holding time is six months.

Level C personnel safety protection is recommended. The decontamination location should be outside of the sampling zone.

The estimated total cost for sampling is \$ 11,640. The estimated cost per sample is \$ 155. Sampling time is estimated to be three days.

NOTICE

Although research described in this article has been funded wholly or in part by the United States Environmental Protection Agency under contract number 68-03-3249 to Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute Agency endorsement of the product.

DISCUSSION

TOM PRITCHETT: What you're doing is extremely critical. We have people at EPA in the field crying for this information and some type of guidance. We literally need it yesterday in the field. We can't afford to wait a year or two years to get it through approval processes. What you're doing is outstanding work. I just hope we can see it in three months.

ROMAN OLIVERO: We are an EPA contractor, and how to get this through the system is up to EMSL-Las Vegas. That's why we have a phased approach to testing. You might get it in two months, after in-house testing, or in six months after review. The product quality of what you get will depend on the testing level.

DON FLORY: Do you have built into this decision-making system typical precisions for different matrices for the different analytical methods?

ROMAN OLIVERO: We are addressing metals and cyanide in a soil matrix, and we have published typical precision and accuracy for the metals.

There are no data on sampling precision and accuracy. The other half of the coin in still remiss, and EMSL is working toward that. But just knowing how good your analytical method is in the lab may not be enough, your sampling error could outweigh that. So that doesn't mean much, really.

DON FLORY: Could I change the data base, then, and put some new numbers in?

ROMAN OLIVERO: Since we have a lack of data in many areas, we're thinking of providing a way for people to change, update those numbers, or provide those numbers we don't have, as they become available. It's not in the system right now, but we have pretty much decided we will do that.

DON FLORY: Let me suggest strongly that you do that. For one example, if we have a demonstration phase for a project, and we take a lot of samples and get QA/QC data, and then we want to put those into the remediation plan, we can have real data–real precision and accuracy for those kinds of samples in those matrices. We should be able to put those in, so we can make that next step.

The other question is can we put the cost analyses in and compare data quality objectives, then, to total cost? You're calculating all of the numbered samples and everything we need to run, and we would need to be able to do that, also. That would be very helpful.

ROMAN OLIVERO: Yes, two of the models that we're developing last are DQO and budget, the most important ones. The techniques were there in the documents. We plan to provide a way for users to, in an interactive way, change their DQO's and the money available, so they can get them to match.

DON FLORY: Did you say how big a computer, how big a memory, what kind of computer this will run on?

ROMAN OLIVERO: It was developed on Knowledge Pro, which is an IBM-PC based development tool for expert system. It runs on an IBM-PC or any compatible. We have it in a self-powered portable here, which can be taken into the field. You need 640K to run it.

Running off a hard drive is a lot faster, even though we run it off here, and it runs on color or monochrome. You need a printer to get recommendations. They are shown on the screen, but of course you want to print it, and you can use an optional mouse pointing device.

DON FLORY: You have been running it off the floppies?

ROMAN OLIVERO: We have it on hard drive but it can be run off floppy disks. There are no royalties that we need to pay to either Bolan or to Knowledge Garden for Knowledge Pro. You get a one-time system, and you don't need anything else in your computer, any other software, or anything to run it. It's self contained.

DELYLE EASTWOOD: We are having a meeting to discuss an ASTM guidance document on field operations this evening. It's a very preliminary document. I'm sure there are a lot of mistakes in it, but at least it's a start. EPA is also working on guidance documents. Obviously there is a need for both expert systems and guidance documents, and I hope that there is some way to update the data in these expert systems. I did see one or two things on your slide that I would disagree with.

Some of the points are debatable, but I think there's a need for both guidance documents and expert systems, and I hope people will come to the discussion of this ASTM field and laboratory operations document, because we need all the input we can get.

ROMAN OLIVERO: Yes, we need documents and expert systems. We need the input of the people. We obtained all the documents we could, and we have some good experts, but we're just a little tiny piece of knowledge available out there. If you can contribute with either document references, even unpublished information, or your own expertise somehow, please contact us. We would like to work with you.

JONATHAN NYQUIST: Once you've gotten your recommendation, can the user get a dump of the rules that we used to reach that decision?

ROMAN OLIVERO: We're working on implementing a feature. That's called a Y feature. It's very hard on this tool, but definitely we do need that.

INTRODUCTION TO THE SESSION ON OTHER ADVANCED FIELD TECHNIQUES

RONALD MITCHUM, CHAIRPERSON

The other techniques in this session are a very diverse group of topics, going all the way from purge and trap, GC/MS, to short-term bioassessments, or biomonitoring at Superfund sites, all the way down to EPA field screening projects.

I would talk to you just a minute or two about the philosophy that I have regarding field screening techniques. That might set the stage for these other categories, the other techniques that maybe next year will be even bigger.

I had some definite ideas about field screening and what it should be. One of the problems that we have is it may be fast and cheap, and not give an answer. In field screening techniques, we need to look at the purpose for having them.

We did this so we can obtain data in the field, at a somewhat faster rate than we could by sending it out to some laboratories that service us.We did it so we might even have some of the same quality assurance that we have in some of these other laboratories, so the data would have some meaning.

But what is the question that we're trying to ask in the field? In many cases, the question is not a quantitative question. The question is a yes-no question. In many cases if I could say that there is not one of the NPL compounds at this site, we could save ourselves a lot of trouble.

But unfortunately, many of our screening techniques are very specific techniques, rather than the general technique that would answer that broad question.

What's more important? To us in the EPA, zeros are very important, because most of the numbers we get are zeros. Our ability to measure zeros is very important. Our ability to measure gangs of zeros is even more important.

An example of that is the Love Canal habitability study. We took 1300 dioxin samples around houses and in ditches. We analyzed all 1300, and we had one positive hit.

That tells you something about the way that we look at samples coming out of the field. If we had a very good way to obtain zeros, then we would have had a very good way to do 1300 samples very effectively, and a very lousy way to have done one.

In many cases, that's very important, and in many cases, this is the question you might consider in the future. How do we get good zeros? What are some of the methods for doing that?

Another philosophical issue about field screening techniques is what kind of technologies do we put out there? We see some very good, innovative approaches to doing field measurements – that's fieldable technology, versus package or single-person technologies.

In many cases, we're dealing with answering the same questions in a little different way. What's the most cost effective way for us to do that? It's more cost effective for me to take a GC in the field in a truck than it is for me to fund the development of a GC I can carry in my hand. You've got to consider those kinds of things when you look at fieldable technologies.

Give me a method that will measure me a zero, and I'll make you a millionaire. Give me a method that will measure one compound, and I'll guarantee you to fail, because we've never asked one question at a time. We always ask more than one question in chemistry, so you've got to always consider that, also, in your development efforts. How many questions do we ask?

In many cases, you've also got to take a look at how and what was the history behind the development of technologies and chemistry, and that's what we're talking about.

In many cases, chemistry was developed for a different reason than for field applications. So you take a look at the route of the technique, and say, now how do I address that and make it go to the field? Don't take it as such and say, I've got to take this $150,000 mass spectrometer to the field some way. It wasn't designed to do that, and it's also not answering the question you want it to answer.

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EVALUATION OF A FIELD-BASED, MOBILE, GAS CHROMATOGRAPH-MASS SPECTROMETER FOR THE IDENTIFICATION AND QUANTIFICATION OF VOLATILE ORGANIC COMPOUNDS ON EPA'S HAZARDOUS SUBSTANCE LIST

Albert Robbat, Jr. and George Xyrafas
Tufts University, Chemistry Department
Trace Analytical Measurement Laboratory
Medford, Massachusetts 02155

ABSTRACT

A gas chromatograph-mass spectrometer (GC-MS) has been evaluated for the analysis of volatile organic compounds (VOCs) on EPA's Hazardous Substance List. The gas chromatographic separation of thirty-five VOCs on a DB624 capillary column using ambient air as the carrier gas was excellent. A wide linear dynamic range for the mass spectrometer was obtained for each compound with minimal detectable quantities (10ng) at the level required for hazardous waste site investigation. The GC-MS was transported in a Chevrolet Blazer for field investigations of suspected chlorinated VOC contamination in tap water and in groundwater. Field and laboratory measurements are intercompared.

Key words: field gas chromatograph-mass spectrometer, groundwater contamination, on-site field investigations.

INTRODUCTION

In November, 1986, the citizens of Massachusetts voted by referendum overwhelmingly to amend the state's Superfund law and require the state's Department of Environmental Quality Engineering (DEQE) to list by January 1987, 400 hazardous waste sites that will be investigated; at least 600 additional sites by January 1988, and a minimum of 1000 new hazardous waste sites each year thereafter. The law stipulates well-defined timetables for classification, remediation and disposition of listed sites. For example, "priority sites" must be fully evaluated and a permanent remedy must be completed within four years (technology permitting), or be temporarily secured, and/or capped. "Nonpriority sites" must be fully evaluated and have an action plan instituted within seven years of site listing. To meet this most difficult and costly timetable, it is becoming increasingly important to develop new, on-site, analytical instrumentation which can identify and quantify environmentally important compounds. Field technology that can provide unambiguous identification and quantification of chemical contaminants should provide site managers with analytical data necessary to make immediate decisions. Moreover, on-site decision-making should result in improved deployment of field personnel and equipment and should result in increased cost savings. This is due to the fact that commercial and state laboratories currently experience a two-to-four month lag time between field sample collection and production of laboratory results.

A new gas chromatograph-mass spectrometer (GC-MS), designed specifically for field investigations, has been evaluated for volatile organic compounds (VOC) found on the U.S. EPA's Hazardous Substance List (HSL). In this report, the high resolution, capillary DB624, separation of the HSL VOCs are presented. In addition, the linear dynamic range, the minimum detectable quantities, and the selectivity of the field GC-MS toward VOCs present in aqueous solutions have been investigated. Finally, field GC-MS, laboratory GC-MS, and laboratory GC-ECD results are intercompared for the determination of trichloroethene and 1,1,1-trichloroethane found in home drinking water.

EXPERIMENTAL SECTION

The Bruker Instruments GC-MS used in this investigation has been described in detail in another paper presented at this symposium (Trainor and Laukien). The GC was equipped with an automated thermal desorption oven.

In this study a 30m x 0.32mm i.d. fused silica capillary column coated with 1.8μm film of DB624 was used. The optimum gas chromatographic operating condition for on-site measurements during summer conditions was established for the separation of all HSL VOCs simultaneously: viz.; 28 °C isothermal for seven minutes followed by linear temperature programming at 7 °C/min to 120 °C. The final temperature was held constant for 7 min. The carrier gas was ambient air flowing at 1 ml/min. The mass range scanned was between 45 amu and 260 amu with a 2 sec scan time. The area under each VOCs primary m/z ion was used in the quantitation calculations as specified by EPA procedures. Data acquisition was delayed for 3.7 min from the start of compound desorption into the GC.

The linear dynamic range was established by using known concentrations of standard solutions from Supelco. Six standard solutions were made (in methanol) containing compound concentrations of: standards 1) 1000 ng/μl; 2) 4000 ng/μl; 3) 5000 ng/μl;

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4) 10,000 ng/μl; internal standard 5) 2000 ng/μl full scan MS; and 6) 4000 ng/μl SIM. Standard solutions were injected into a tube containing 150 mg of Tenax. The tube was placed into the GC desorption oven maintained at 220 °C for 45 sec. The actual GC experiment began immediately after the 45 sec sample desorption period. Standard solutions were serial diluted and appropriate quantities injected into a new tube. The procedure was continued until GC-MS signals resulting from these compounds were no longer observable.

Figure 1 illustrates the sample preparation technique employed in the drinking water experiments for VOC analysis. The water solution was purged with ambient air using a Gillian (model 513) air sampling pump with the VOCs trapped in a tube. Eighty ml drinking water samples were used (sparged for 5 min at 0.5 l/min) with the VOCs collected on 150 mg of 50/50 Tenax/charcoal.

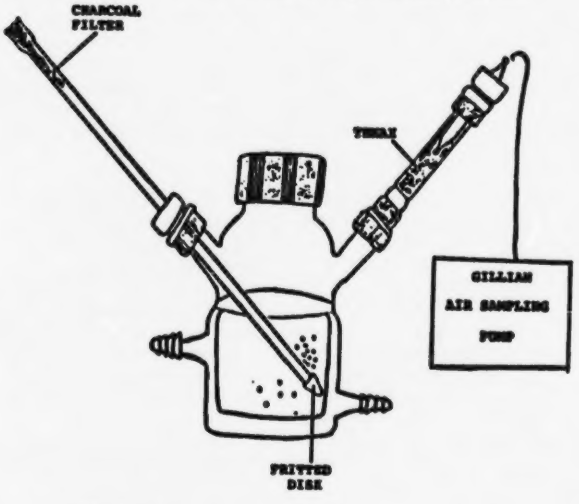

Figure 1.
Purge and Trap Sampling Vessel.

Home drinking water investigations were performed in cooperation with DEQE and the town's water department. Personnel from DEQE collected the tap water according to standard practice. The drinking water samples were analyzed by us (field GC-MS), town (laboratory GC-ECD), and DEQE's Lawrence Experiment Station (laboratory GC-MS). DEQE performed VOC analyses of the water samples as prescribed by EPA method 524. Headspace (volume 1 cc) GC-ECD experiments were performed by town personnel on an instrument manufactured by Analytical Instrument Development Inc. linked to an integrator. A 6 ft x 1/8 in stainless steel column containing 1% SP1000 was maintained at 185 °C. The carrier gas consisted of 5% methane in argon at a flow rate of 40 ml/min. Sample preparation consisted of agitating a 30 ml aliquot of the tap water sample for 1 minute before analysis.

Since the GC-MS and sample sparging technique utilized air from the site as the carrier gas, background signals at the site were evaluated by performing GC-MS experiments on Tenax/charcoal collected samples from 80 ml of purified water (blank) and standard solutions containing known concentrations of chlorinated VOCs in 80 ml of purified water at the beginning, middle, and end of the days' experiments. The GC-MS operating conditions and sample preparation procedures have been described above with the exception of the GC column temperature employed. The GC oven was maintained at 30 °C for 11.7 min, linearly ramped 10 °C/min to a final temperature of 124 °C. The final temperature was held constant for five minutes. The data acquisition delay time was 2.8 min.

RESULTS AND DISCUSSION

Well-defined GC-MS operating conditions (see experimental section) were established keeping in mind the need for developing on-site analytical tools capable of identifying the wide molecular diversity of the VOCs on EPA's hazardous substance list. Figure 2 illustrates the high resolution gas chromatographic separation of 31 of the 35 VOCs. The peak numbers correspond to compound numbers identified in Table 1. The concentration of each compound injected was 200 ng. The excellent chromatographic separation was obtained on a 30m x 0.32mm i.d. fused silica capillary column coated with a 1.8μm film of DB624. Although some of the compounds coeluted, all of the VOCs can be differentiated based on their mass spectrum.

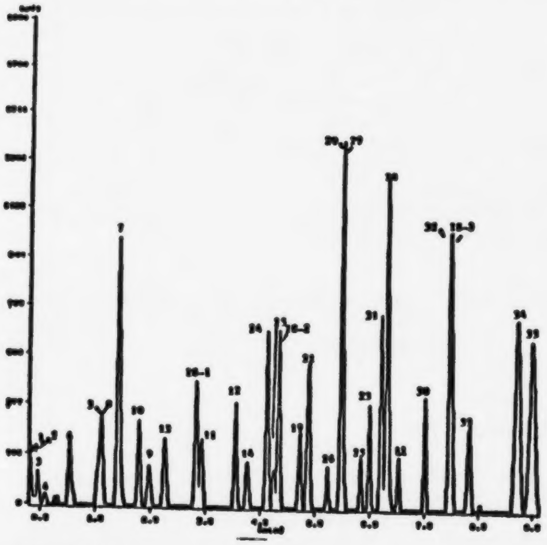

Figure 2.
Field GC-MS of a methanol solution containing a standard mixture of volatile HSL compounds on a DB624 capillary column. Peak numbers correspond to compounds listed in dynamic range table.

The GC-MS full scan linear dynamic range toward the VOCs was evaluated within wide concentration ranges by preparing standard solutions containing different initial concentrations as specified in Table 1. The selected ion monitoring (SIM) linear dynamic range for some chlorinated VOCs revealed that the dynamic range could be extended by a factor of about ten. Generally, the full scan MS detection limits are within the useful analytical range for hazardous waste site assessment. The minimum detectable quantity (at S/N=3) for identification purposes was between 10ng and 40ng of compound injected for full scan MS and

Table 1. HSL VOC Identity and Linear Dynamic Range for Field GC-MS.

#	Compound	full scan MS(ng)	r	SIM (ng)	r
1.	Chloromethane	100-10,000^{d}	0.999		
2.	Bromomethane	100-10,000^{d}	0.994		
3.	Vinylchloride	100-10.000^{d}	0.999		
4.	Chloroethane	100-10,000^{d}	0.996		
5.	Methylene chloride	40-400^{a}	0.998		
6.	Acetone	40-4,000^{b}	0.993		
7.	Carbon Disulfide	40-4,000^{b}	0.975		
8.	1,1-Dichloroethene	40-400^{a}	0.997		
9.	1,1-Dichloroethane	40-1,000^{a}	0.996	10-1000^{f}	0.998
10.	1,2 Dichloroethene	100-1,000^{b}	0.999	4-1000^{f}	0.999
11.	Chloroform	40-1000^{a}	0.996	10-1000^{f}	0.998
12.	1,2-Dichloroethane	40-1000^{b}	0.999		
13.	2-Butanone	40-4,000^{b}	0.991		
14.	1,1,1-Trichloroethane	100-1000^{b}	0.999	4-1000^{f}	0.995
15.	Carbon tetrachloride	100-1000^{a}	0.997	10-1000^{f}	0.999
16.	Vinyl acetate	did not quantify			
17.	Bromodichloromethane	40-5000^{c}	0.999		
18.	1,1,2,2-Tetrachloroethane	100-5000^{c}	0.998		
19.	1,2-dichloropropane	40-1000^{a}	0.990		
20.	trans 1,3-Dichloropropene	40-5000^{c}	0.998	4-1000^{f}	0.996
21.	Trichloroethene	40-1000^{a}	0.983	10-1000^{f}	0.998
22.	Dibromochloromethane	40-1000^{a}	0.995		
23.	1,1,2-Trichloroethane	40-1000^{a}	0.997		
24.	Benzene	40-1000^{b}	0.999		
25.	cis-1,3-Dichloropropene	40-5000^{c}	0.997		
26.	2-Chloroethyl Vinyl Ether	did not quantify			
27.	Bromoform	400-5000^{c}	0.999		
28.	2-Hexanone	40-4000^{b}	0.976		
29.	4-Methyl-2-pentanone	40-4,000^{b}	0.990		
30.	Tetrachloroethene	40-1000^{a}	0.983		
31.	Toluene	40-5000^{c}	0.998	4-1000^{f}	0.996
32.	Chlorobenzene	40-400^{a}	0.998		
33.	Ethylbenzene	40-5000^{c}	0.996		
34.	Styrene	did not quanitify			
35.	Total Xylenes	did not quantify			
	internal standards				
1.	Bromochloromethane	20-2000^{e}	0.998		
2.	1,4-difluorobenzene	20-2000^{e}	0.998		
3.	Cl-benzene-d5	20-2000^{e}	0.991		

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initial concentration (ng/μl) of standard solutions before dilution

^{a}1) 1000
^{b}2) 4000
^{c}3) 5000
^{d}4) 10000
^{e}5) 2000 (internal standard)
^{f}6) 4000

about twenty-five times more sensitive by SIM. The MS displayed a linear response within the concentration ranges studied. It should be recognized that the upper limits and minimum detectable quantities are strongly dependent upon the GC operating conditions and primary ion MS signal strength. For some compounds, the upper limit was restricted due to poor chromatography. Because HSL compounds represents a target list of environmentally important organic compounds having widely different molecular structures, such diversity of compounds will have varying selectivities on a given stationary phase under differing experimental conditions. The dynamic range data was based on a single GC-MS operating condition for all of the VOCs studied (versus a number of operating conditions optimized for various compounds, e.g., chlorinated hydrocarbons or gasoline constituents, benzene, toluene, and xylenes) and was specifically optimized for on-site, field investigations which might be performed in varying climatic conditions.

The GC-MS response factor, RF, and percent standard deviation for twelve chlorinated VOCs problematic in contaminated waters were determined. The average value reported in Table 2 was calculated from experiments performed at five different concentrations between the range of 20 and 200μg/l. Each set of experiments was repeated three times. Response factors were calculated using 50 ppb of 1,4-difluorobenzene as the internal standard. The data reveal that the GC-MS responded within the error tolerances accepted for commercial laboratory analysis. Figure 3 illustrates a typical GC-MS total ion current chromatogram of a standard chlorinated VOC mixture containing 100 μg/l of compound sparged from purified water.

Table 2.

Average Response Factor and Percent Standard Deviation for Some Chlorinated VOCs.

#	Compound	RF	%SD
1.	vinyl chloride	0.042	16.5
2.	1,1-dichloroethene	0.302	9.9
3.	methylene chloride	0.452	15.7
4.	trans-1,2-dichloroethene	0.392	12.7
5.	1,1-dichloroethane	0.337	21.0
6.	cis-1,2-dichloroethene	0.418	12.6
7.	chloroform	0.271	14.4
8.	1,1,1-trichloroethane	0.109	12.1
9.	carbon tetrachloride	0.062	22.6
10.	1,2-dichloroethane	0.432	16.9
11.	trichloroethene	0.429	15.5
12.	tetrachloroethene	0.722	17.0
1,4-difluorobenzene internal standard, IS			

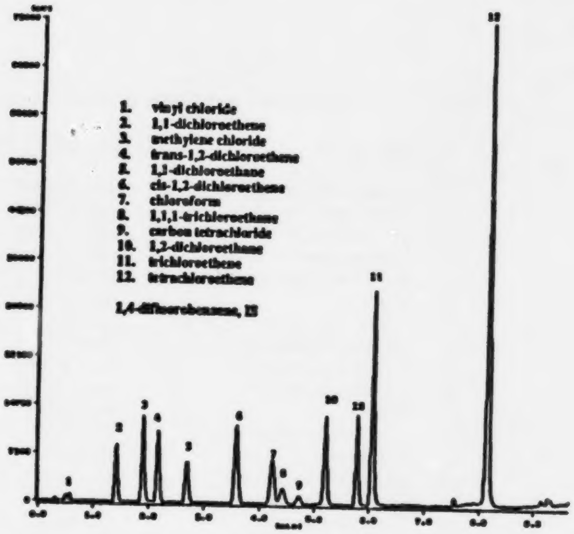

Figure 3.

GC-MS response toward a standard mixture of twelve volatile chlorinated HSL compounds.

The GC, MS, and column (over several months) exhibited remarkable stability and consistently excellent separation and quantitation. These characteristics were obtained despite the use of semipurified ambient (charcoal filtered vs. cylinder) air as the carrier gas and the drastically changing climatic conditions, e.g., rain, high humidity and temperature.

On-site evaluation of the mobile GC-MS was performed in cooperation with DEQE personnel, homeowners having chlorinated VOC contamination in their drinking water, and the town's chemist. Drinking water is supplied by each homeowner's well. Based on data from an earlier study, DEQE field personnel collected samples (July. 1988) from about a dozen homes anticipated to have chlorinated VOC concentrations above the maximum allowable levels for trichloroethene (TCE) and 1,1,1-trichloroethane (TCEA). Split samples were analyzed by DEQE's laboratory (GC-MS), the town's laboratory (GC-ECD), and by the authors. The results are presented in Table 3. The trichloroethene intercomparative measurements are in excellent agreement. The comparative measurement for samples in which we detected TCEA was quite good however, we did not detect TCEA in every sample that the laboratory techniques identified this compound in. The nondetection of TCEA in some samples was quite surprising and unexpected since concentration levels were approximately the same as those samples found in the other samples. Moreover, the TCEA dynamic range encompassed the concentration levels of TCEA in the samples. Further studies with the field GC-MS at the laboratory involving TCEA revealed no apparent reason why we should not have detected this compound in homeowner samples. Figure 4 represents a typical GC-MS total ion current chromatogram of the tap water obtained from one of the homes investigated (DEQE sample #18). Inspection of the figure illustrated the

Table 3.

Comparison of Field and Laboratory Measurements for the Analysis of Trichloroethene and 1,1,1-Trichloroethane (PPB).

TRICHLOROETHENE

DEQE #	Field GC-MS	Lab GC-MS	Lab GC-ECD
15	27	27	30
18A	ND	ND	<1
18	48	45	51
20	6	4	5
21	31	28	33
22	21	14	17
24	5	8	10
36	2	2	2
37	12	12	13
38	25	27	30
39	10	10	10
53	ND	ND	<1

1,1,1-TRICHLOROETHANE

DEQE #	Field GC-MS	Lab GC-MS	Lab GC-ECD
15	8	9	8
18A	ND	ND	<1
18	40	49	40
20	ND	<1	1
21	12	8	10
22	9	4	5
24	ND	5	3
36	ND	<1	<1
37	ND	5	18
38	ND	8	8
39	ND	4	4
53	ND	ND	<1

presence of additional chlorinated hydrocarbons: 1,1-dichloroethene (2 ppb), 1,1-dichloroethane (14 ppb), cis-1,2-dichloroethene (8 ppb), and tetrachloroethene (4 ppb).

The field GC-MS measurements allowed decision-makers to make same day recommendations (results from the laboratory were obtained September, 1988). It is evident from the data presented (see also reference 2) that the field GC-MS instrument, under the experimental conditions specified, is well-suited for identifying and quantifying HSL VOCs on-site. The overall remarkable agreement between laboratory and field measurements suggests that this instrument can be used to perform site characterization studies of VOCs in aqueous solutions and in air. Work is in progress to assess the Bruker GC-MS capabilities for HSL VOCs present in soil and sludge. Studies related to semivolatile organic compounds in various matrices have been initiated.

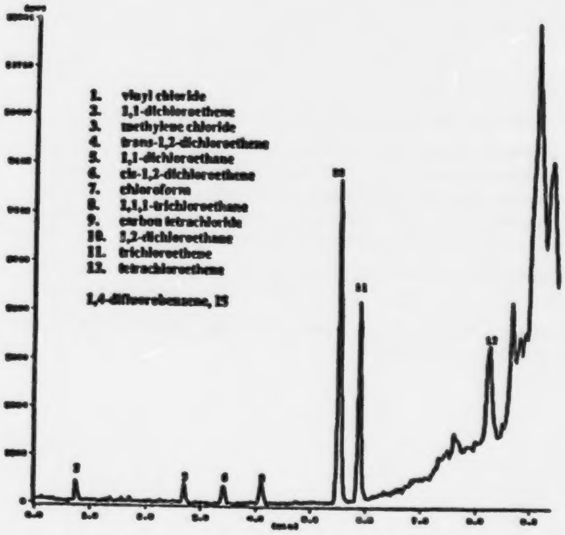

Figure 4.
GC-MS of VOCs found in tap water, DEQE smple #18.

ACKNOWLEDGEMENT

The authors thank Bruker Instruments for use of the GC-MS instrument and Chevrolet Blazer as well as the many technical discussions related to this work. The authors also thank Lynn Chappel, DEQE, for coordinating the site investigation, and Alan Khafkart, Littleton Water Department, for access to their data. The authors greatly appreciate the help and interest of many other DEQE personnel for allowing us to participate in this and other environmentally important site investigations. Without their help it would have been nearly impossible to gain access to appropriate sites.

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DISCUSSION

JOE SOROKA: How did you define your minimum detection limits?

AL ROBBAT: The minimum detection limit was simply determined by doing the dilution series and getting to the point where we could no longer observe the signal at a signal-to-noise ratio of three to one. What that means is that those points did not necessarily fall on the dynamic range. We use it for two different purposes. One is for screening and secondly to determine presence or absence.

JOE SOROKA: So the detection limits you have listed were three times the signal to noise, whereas the linear dynamic range is significantly higher?

JOE ROBBAT: I wouldn't say significantly higher. I would say maybe one more signal to noise higher.

RONALD MITCHUM: Regarding the HNU you described, was that a GC? Did you measure surface emissions with this Bruker GC/MS, and the little probe, and try to match that with what you saw in the wells in that one study? What was the source of the chlorinated hydrocarbons in the lab study that you did?

AL ROBBAT: To the first two questions, no and no. The source was a semiconductor company that occupied that particular site. It's purported that they were dumping solvents into the stream. That company has since gone out of business.

ION MOBILITY SPECTROMETRY FOR IDENTIFICATION AND DETECTION OF HAZARDOUS CHEMICALS

Julio Reategui
Project Engineer

Tad Bacon
Senior Engineer

Glenn Spangler
Principal Engineer

Joseph Roehl
Marketing Mgr.

Environmental Technologies Group, Inc.
1400 Taylor Avenue
Baltimore, Maryland 21284-9840

ABSTRACT

This paper describes an Ion Mobility Spectrometry (IMS) System which has been designed to detect organic vapors in ambient air as might be required to survey and characterize hazardous waste sites. The system allows real-time identification of chemical vapors and determination of their concentration by generating and interpreting spectral data. The array of applications suitable for this detection system will be discussed.

INTRODUCTION

Growing public concern and regulatory issues relating to air, ground and water quality have created a need to accurately and rapidly assess exposure to hazardous chemicals. Similarly, the process industry continually seeks ways to control purity of materials using real-time trace chemical detection techniques to adjust parameters. New developments in biotechnology, integrated circuit manufacturing, communications, and materials manufacturing have resulted in trace chemical detection requirements that did not exist five years ago. These trends are expected to continue through the next decade.

Presently, a number of analytical technologies such as gas chromatography, mass spectrometry, and various ionization and photo absorption techniques are used to detect, identify and quantify these chemicals. Each of these technologies, however, has limitations, and no single instrument is suitable for all monitoring and detection applications. Furthermore, the choice of instrument or technique depends upon the application, which sometimes involves conflicting requirements. This increasingly complex problem presents a formidable challenge to the chemical detection industry. Together with these needs, the customer desires small, cost-effective and easy to operate instrumentation.

ION MOBILITY SPECTROMETRY - HOW IT WORKS

IMS was developed in the late 60's by the Franklin GNO Corporation as a Laboratory instrument for analysis of trace concentrations of organic compounds. Early on, the potential of this technique was recognized as a method of identification for extremely low levels of chemicals. Advances in technology since that time have resulted in miniaturization of the IMS detector cell, and the required electronics/data processing systems. These improvements, along with the introduction of a membrane inlet system and a recirculating air purification system, have made IMS practical for ambient air monitoring. The resulting instrument is small, rugged and requires little routine maintenance.

The principle of IMS is illustrated in Figures 1 to 4. Ambient air is drawn into the instrument and past a semi-permeable membrane on the outside of the cell by use of a sampling pump. The membrane allows materials of interest to pass into the detection cell, while attenuating many possible interferents. Purified dry air from a self-contained scrubbing system sweeps the membrane on the inside of the cell and delivers the sample to the reaction region. There the sample, consisting of one or more components, is ionized by reactions with a weak plasma of positive and negative ions, formed by ionization of the purified air by a radioactive source. The ionized sample molecules and reactant ions drift through the cell under the influence of an applied electric field. A shutter grid allows periodic introduction of the ions into a drift tube where they separate based on charge, mass, and shape. Smaller ions move faster than larger ions through the drift tube and arrive first at the detector. The ability of an ion to move through another gas is called "mobility". Because different ions have different mobilities, the ions arrive at the collector with different drift times. The current created at the detector is amplified, measured as a function of time, and a spectrum is generated. The identity of the molecules can then be determined using pattern recognition algorithms using a computer or microprocessor to analyze and compare features of the IMS signature with information stored in memory. The electric field is periodically reversed so that ions of both polarities can be studied. A general purposes IMS based detection system (GPIMS) is illustrated in Figures 5 to 9.

Specificity is a function of the success with which the detection algorithm recognizes specific compounds by their unique mobility spectrums. Additional specificity might also be obtained for certain compounds by membrane selection or using dopant vapors in the carrier gas, changing the ionization chemistry.

Figure 10 illustrates the ability to detect a specific compound in the presence of high concentrations of possible interferences. In this example, TDI is given as the target compound, detected in the negative mode. Even saturated headspace vapors of chlorobenzene, 2-propanol, and ammonium hydroxide do not interfere with the detection of TDI. The response of these materials occurs in the positive mode (not shown) and could be identified. Phosgene is detected in the negative mode, and so also appears along with the TDI, and is identified. In field screening applications, the instrument can be operated as a general class detector or as a specific detector. In the general class mode, the unit distinguishes, for instance, halogenated compounds which produce negative ions, and compounds such as ketones, esters, alcohols, ethers, etc. which produce positive ions. In the specific mode, the instrument can identify the specific compounds on the basis of their mobilities. Semi-quantitative results are available for both modes of operation. Under controlled conditions, the instrument also may be calibrated to produce accurate quantitative results.

Since IMS responds to a variety of chemical vapors, an IMS detection system can be reprogrammed to detect new chemicals without any hardware modification and reject new interferents as they arise. This could provide a great savings for those who use a detection system that needs to respond to changing requirements or threats.

As a result of the ion mobility separation process, IMS is more specific than other types of ionization detectors, and less prone to false alarms. IMS combines the simplicity and sensitivity of ionization detectors with the additional degree of specificity gained from interpretation of IMS' spectral data through detection algorithms. It, therefore, bridges the gap between the nonspecific screening devices and elaborate analytical instruments.

It is a versatile and a sensitive real-time trace vapor detector. Because of its small size and minimal system requirements, IMS is ideal for use as a cost-effective fixed or portable chemical detector. Detectors based on IMS provide real-time analysis (usually within 5 seconds); they are small enough to be hand-held; inherently more rugged than a GC or MS; very sensitive (in the sub-ppb range); and can be trained to detect, identify and estimate concentrations of many chemical compounds. These relationships are illustrated in Table 1.

IMS systems are unique among chemical detectors in that their detection capabilities can be enhanced for specific applications through simple operating parameter modifications. Overall, IMS systems offer technical and logistical advantages that make them attractive as chemical vapor detectors for a wide variety of application in commercial, industrial and military markets.

APPLICATIONS OF ION MOBILITY SPECTROMETRY

The potential commercial and industrial applications for IMS technology include the following:

- Field detection and identification of predetermined target chemicals for chemical processing industries.
- Pre-screening of samples prior to laboratory analysis to determine relative levels of contamination. This would speed up sample preparation times, and reduce down time due to oversaturated analytical instruments.
- Screening detector for quick examination of hazardous waste dumps, for specific chemicals or groups of chemicals.
- Environmental monitoring systems, such as networks of detectors positioned around chemical factories and chemical agent demilitarization sites.
- Trace contaminant detection in controlled chemical processes (used in clean rooms and chemical production facilities).
- Portable, hand-held chemical leak and spill detectors suitable for use in emergency situations.
- Tandem detectors, such as GC/IMS and IMS/MS, to be used as analytical tools to support research performed in government laboratories, universities and institutions.

Chemicals that can be detected by IMS systems are listed in Figures 11 and 12.

SUMMARY

In summary, IMS is an especially attractive technology for instruments used in field screening applications. It may be used as a class detector or to identify specific chemicals. The instrument provides sensitivity in the PPB to PPM range in real-time (<5 sec.).

ACKNOWLEDGEMENTS

Special thanks are extended to Dr. Joe Epstein; Dr. David Lubman of the University of Michigan, Ann Arbor; and Dr. Len Luskus from Brooks AFB, Texas, who reviewed the text and provided valuable comments during the preparation of this paper.

The authors also wish to express their appreciation to Ms. Rita Rosenberger for her skillful typing of the manuscript and Messrs. Bob Allen and Barry Rodgers for their contributions with the illustrations of this paper.

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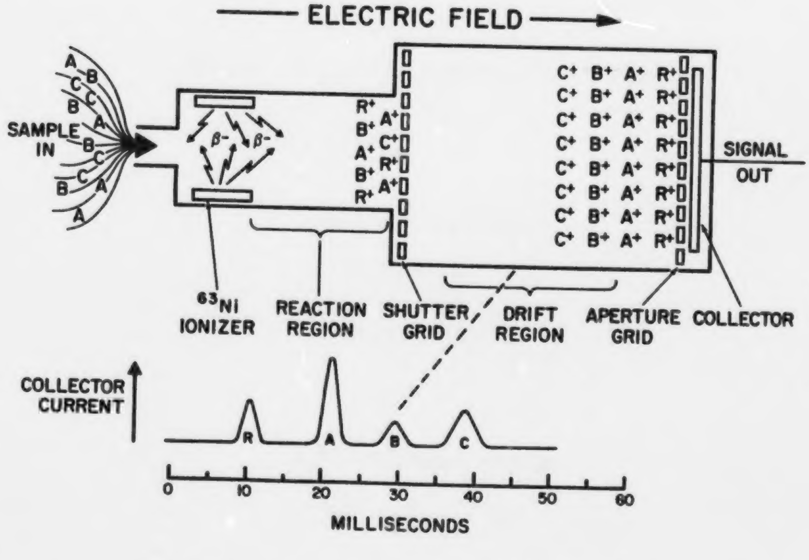

ELECTRIC FIELD
SAMPLE IN
A B C
β^-
R^+ B^+ A^+ B^+ R^+
A^+ C^+ R^+ A^+
C^+ B^+ A^+ R^+
SIGNAL OUT
^{63}Ni IONIZER
REACTION REGION
SHUTTER GRID
DRIFT REGION
APERTURE GRID
COLLECTOR
COLLECTOR CURRENT
R
A
B
C
0
10
20
30
40
50
60
MILLISECONDS

Figure 1. Theory of Operation of IMS Cell

POSITIVE IONS	NEGATIVE IONS
Proton Transfer $RH^+ + P \rightarrow R + PH^+$ Nucleophilic Attachment $R^+ + P \rightarrow RP^+$ Hydride or Hydroxide Abstraction $R^+ + PH \rightarrow RH + P^+$ Oxidation $R^+ + P \rightarrow R + P^+$ Complex Rearrangement	Charge Transfer $R^- + P \rightarrow R + P^-$ Dissociative Capture $R^- + AP \rightarrow R + \dot{A} + P^-$ Proton Abstraction $R^- + HP \rightarrow RH + P^-$ Electrophilic Attachment $R^- + P \rightarrow RP^-$

Figure 2. Ion/Molecule Reactions

$$K = \frac{3e}{16N}\left[\frac{1}{m} + \frac{1}{M}\right]^{1/2} \times \left[\frac{2\pi}{kT}\right]^{1/2} \times \frac{1 + \Delta}{\pi r_m{}^2 \Omega^{(1,1)*}}$$

WHERE

e = IONIC CHARGE

m = IONIC MASS

N = MOLECULAR NUMBER DENSITY

M = MOLECULAR MASS

k = BOLTZMANN CONSTANT

T = TEMPERATURE

r_m = POSITION OF MINIMUM POTENTIAL FOR INTERACTION

$\Omega^{(1,1)*}$ = FIRST ORDER COLLISION INTEGRAL

Δ = CORRECTION TERM FOR HIGHER APPROXIMATIONS

Figure 3. Mason-Schamp Theory For Mobility

DRIFT VELOCITY (V_d)

$$V_d = KE$$

MOBILITY (K)

$$K = \frac{d}{t_d E}$$

REDUCED MOBILITY (K_o)

$$K_o = K \frac{P}{760} \cdot \frac{273}{T}$$

Figure 4. IMS Equations

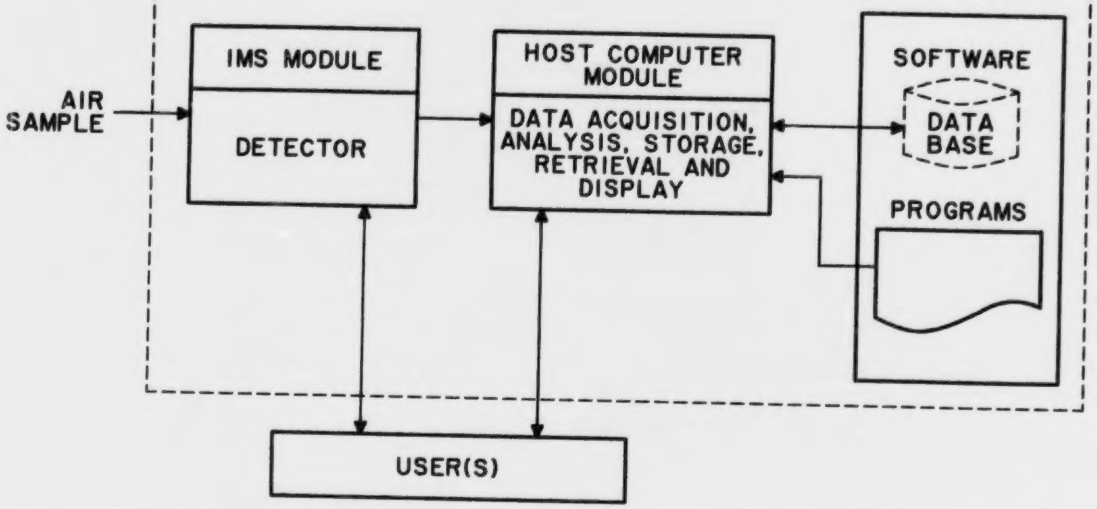
AIR SAMPLE
IMS MODULE
DETECTOR
HOST COMPUTER MODULE
DATA ACQUISITION, ANALYSIS, STORAGE, RETRIEVAL AND DISPLAY
SOFTWARE
DATA BASE
PROGRAMS
USER(S)

Figure 5. General Purpose Ion Mobility Spectrometry System (GP-IMS) for Real-Time Field and Laboratory Evaluation of Chemical Vapors in PPT to PPM Range

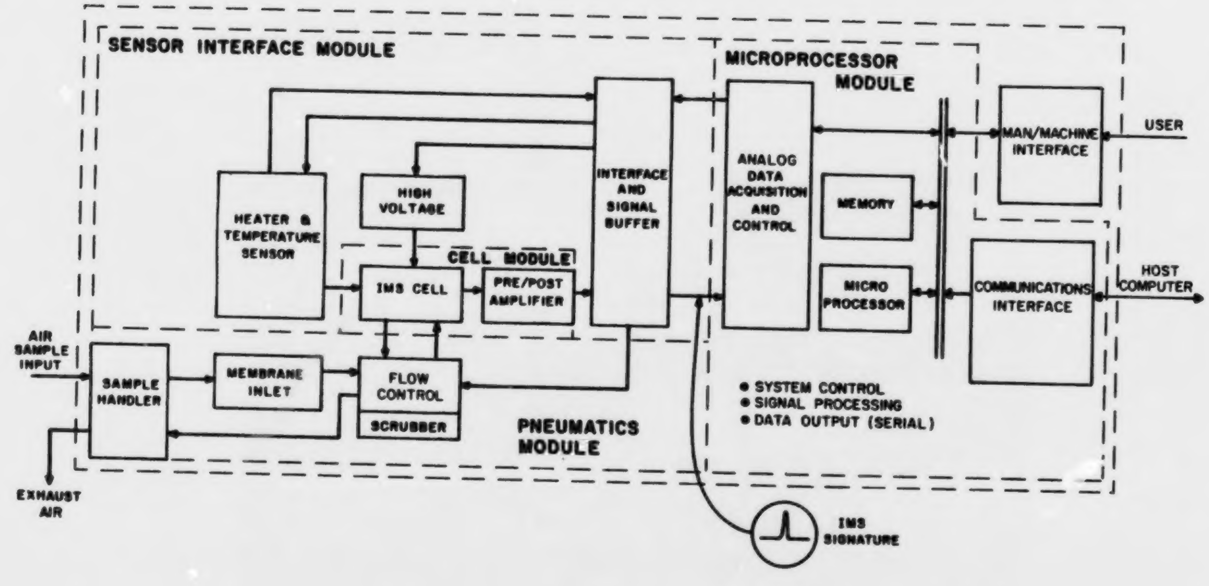
SENSOR INTERFACE MODULE
MICROPROCESSOR MODULE
HEATER & TEMPERATURE SENSOR
HIGH VOLTAGE
CELL MODULE
IMS CELL
PRE/POST AMPLIFIER
INTERFACE AND SIGNAL BUFFER
ANALOG DATA ACQUISITION AND CONTROL
MEMORY
MICRO PROCESSOR
MAN/MACHINE INTERFACE
USER
COMMUNICATIONS INTERFACE
HOST COMPUTER
AIR SAMPLE INPUT
SAMPLE HANDLER
MEMBRANE INLET
FLOW CONTROL
SCRUBBER
PNEUMATICS MODULE
EXHAUST AIR
• SYSTEM CONTROL
• SIGNAL PROCESSING
• DATA OUTPUT (SERIAL)
IMS SIGNATURE

Figure 6. Block Diagram of the GP-IMS

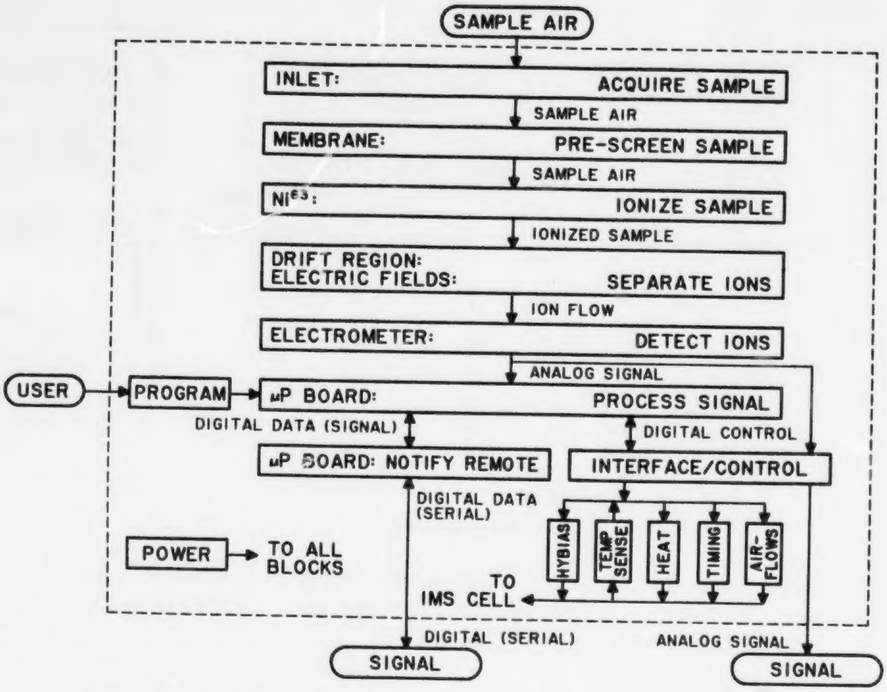
SAMPLE AIR
INLET:
ACQUIRE SAMPLE
SAMPLE AIR
MEMBRANE:
PRE-SCREEN SAMPLE
SAMPLE AIR
NI63:
IONIZE SAMPLE
IONIZED SAMPLE
DRIFT REGION:
ELECTRIC FIELDS:
SEPARATE IONS
ION FLOW
ELECTROMETER:
DETECT IONS
ANALOG SIGNAL
USER
PROGRAM
μP BOARD:
PROCESS SIGNAL
DIGITAL DATA (SIGNAL)
DIGITAL CONTROL
μP BOARD: NOTIFY REMOTE
INTERFACE/CONTROL
DIGITAL DATA
(SERIAL)
HYBIAS
TEMP SENSE
HEAT
TIMING
AIR-FLOWS
POWER
TO ALL
BLOCKS
TO
IMS CELL
DIGITAL (SERIAL)
ANALOG SIGNAL
SIGNAL
SIGNAL

Figure 7. Ion Mobility Spectrometry System Theory of Operation

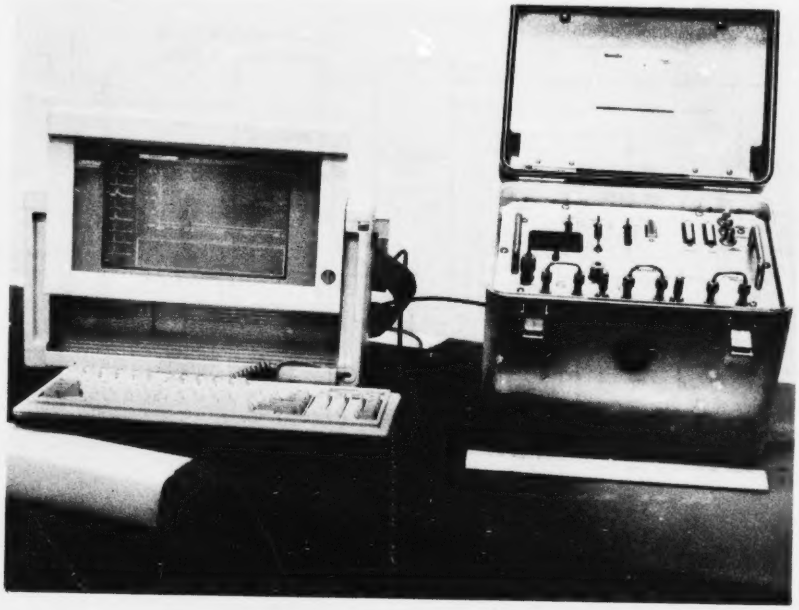

Figure 8. Modular Commercial Detector That Can Be Set to Recognize a Wide Variety of Chemicals

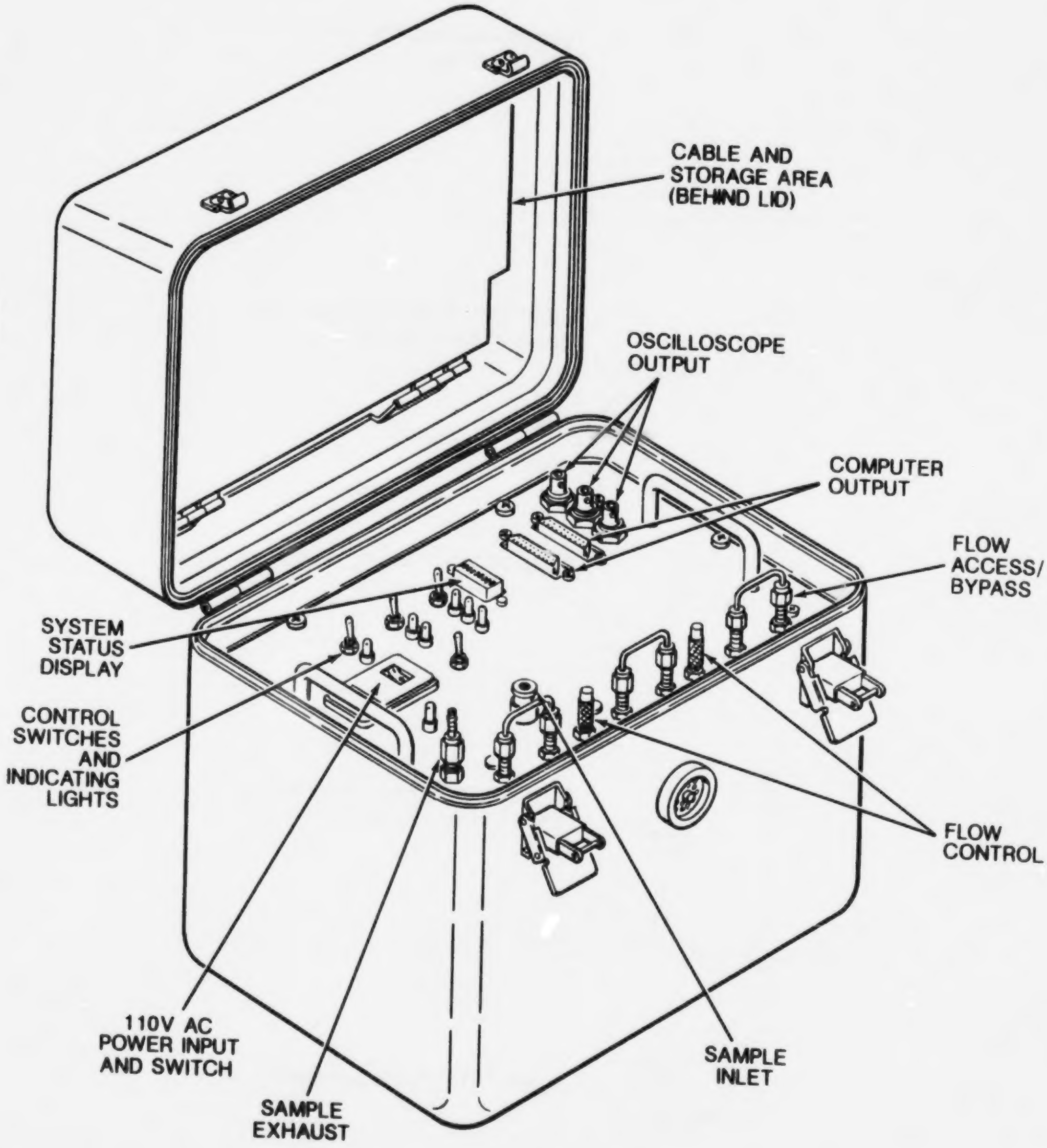
CABLE AND STORAGE AREA (BEHIND LID)
OSCILLOSCOPE OUTPUT
COMPUTER OUTPUT
FLOW ACCESS/ BYPASS
SYSTEM STATUS DISPLAY
CONTROL SWITCHES AND INDICATING LIGHTS
FLOW CONTROL
110V AC POWER INPUT AND SWITCH
SAMPLE INLET
SAMPLE EXHAUST

Figure 9. Ion Mobility Spectrometer

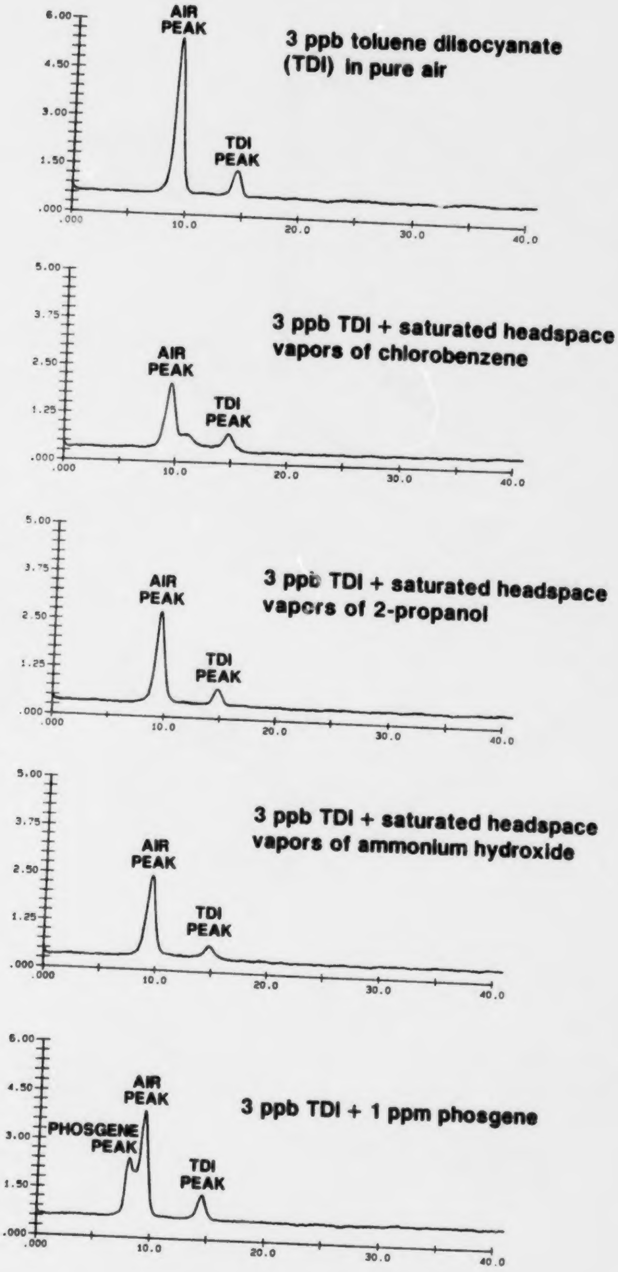

Figure 10. Detection of TDI in the Presence of High Concentration of Possible Interferences

CHEMICALS THAT CAN BE DETECTED BY IMS

- TOLUENE DIAMINE (TDA)
- DINITROTOLUENE (DNT)
- TRINITROTOLUENE (TNT)
- TOLUENE DIISOCYANATE (TDI)
- METHYLENE BIS PHENYL ISOCYANATE (MDI)
- TOLUIDINES
- METHYLENE DIANILINE (MDA)
- VINYL ACETATE
- TETRAHYDROFURAN (THF)
- FORMALDEHYDE
- ACRYLONITRILE
- ACETALDEHYDE
- CYCLOHEXANONE
- ACETONE
- ALCOHOLS
- KETONES
- HALOGENATED COMPOUNDS
- NITRO-COMPOUNDS, EXPLOSIVES
- AMINES
- ESTERS

- ORGANOPHOSPHORUS COMPOUNDS
- DRUGS
- PESTICIDES

- PHENOLS
- ETHYL ETHER
- METHYL ETHYL KETONE
- PYRIDINE
- PIPERIDINE
- HYDROGEN CYANIDE (HCN)
- PHOSGENE
- HYDROCHLORIC ACID (HCl)
- BENZYL CHLORIDE
- NITRIC ACID (HNO_3)
- IODINE (I_2)
- HYDROIODIC ACID (HI)
- PHOSPHOROUS TRICHLORIDE (PCl_3)
- HYDROGEN BROMIDE (HBr)

MANY OTHER NIOSH/OSHA REGULATED CHEMICALS

Figure 11. Chemicals That Can Be Detected By IMS

PROTON AFFINITY SCALE

CLASSES OF COMPOUNDS WHICH IMS CAN DETECT

POSITIVE ION MODE:

Those which give a strong response:

- Pyridines
- Unsaturated Anilines
- Aliphatic Amines
- Phosphines
- α,ω-Disubstituted Alkanes
  - Diamines
  - Aminoalcohols
  - Haloamines
  - Aminoethers
  - Diols
- Imino Ethers
- Quinuclidines
- Amides
- Unsaturated Amines
- Organophosphorous
- Thioethers
- Ethers/Epoxides
- Esters
- Ketones

Those which give a response but which can be easily interfered with:

- Cyano-compounds
- Alcohols
- Aldehydes
- Carboxylic Acids
- Thiols
- Formaldehyde
- Aromatics
- Polyaromatic Hydrocarbons
- High molecular weight alkanes

↑ Increasing Proton Affinity

ELECTRON AFFINITY SCALE

CLASSES OF COMPOUNDS WHICH IMS CAN DETECT

NEGATIVE ION MODE:

Those which give a strong response:

- Quinones
- α-Diketones
- Pesticides (structure dependent)
- Nitro-Compounds
- Isocyanates
- Phenols (particularly with electronegative substituents)
- Thioethers
- Barbituates
- Anhydrides
- Enolates
- Polyhalogenated Aromatics/Biphenyls
- Dioxins
- Carboxylic Acids
- Amides

- Cl_2, Br_2
- NO, NO_2
- Monohalogenated Aromatics
- Halogenated Alkones
- Cyano-Compounds
- Strong Acids

IONIZATION MECHANISMS

- Transfer of e^-
- Proton Abstraction
- Anion Attachment

Figure 12. Detection Capabilities of IMS

TABLE 1. COMPARISON OF IMS WITH OTHER PORTABLE AMBIENT AIR MONITORS

INSTRUMENT	SPECIFICITY	ABILITY TO RESOLVE COMPLEX MIXTURES	SENSITIVITY	RESPONSE TIME	PORTABILITY	PRICE	COMMENTS
Photo-Ionization Detector (PID)	Nonspecific. Detects most organics. Does not identify.	None	Sub PPM	Seconds	Very portable	$5K	Hand-held, easy to use. Gives concentration as "total ionizable compounds". Only indicates if "something" is present.
Flame Ionization Detector (FID)	Nonspecific. Detects all organics. Does not identify.	None	PPB-PPM	Seconds	Portable	$5K	Requires hydrogen. Gives concentration as "total organics". Only indicates if "something" is there. More complicated than PID.
Gas Chromatography	Very good specificity depending on detector used. Specific identification.	Excellent ability to resolve most components in very complex mixtures.	PPB-PPM	Tens of minutes	Fairly portable	$10-20K	Requires library of retention times to identify compounds. Requires bottled gas. Excellent resolution of complex mixtures but lengthy analysis and calibration times, fair sensitivity.
Mass Spectroscopy	Very good specificity in noncomplex matrix. Specific identification.	Poor resolution of complex mixtures.	PPB	Seconds	Large, heavy, complex. Not rugged.	$50-200K	Very good sensitivity, produces complex spectra with EI source. Requires library of spectra. Requires high vacuum pumps, large amount of power. Long set-up time.
IMS	Very good specificity to certain compounds in complex matrix. Specificity can be controlled by membrane dopants, polarity. Specific identification.	Able to identify certain target compounds in a complex mixture but does not provide the resolution of a GC.	Sub PPB-PPM	Seconds	Portable	$5-25K	Very good sensitivity. Very rugged. Very good specificity to certain compounds. Requires library of mobilities. Fast response. Provides similar information as chemical ionization MS but in smaller, cheaper, less complex, easier to use package.

DISCUSSION

HAL STUBER: Is there a molecular weight range for which the field portable instruments or techniques are applicable?

JULIO REATEGUI: Yes, the theoretical molecular weight range is between 15 and 500. However, the instrument works better if the compound is between, say 50 and 200.

TOM PRITCHETT: The coronal discharge atmospheric pressure chemical ionization is probably the best source for ionizing polar compounds – the compounds we have the most trouble analyzing by any other way in air matrices. Toluene isocyanate, for example, is something we make evacuation decisions at detection limits that are three times higher than the TLVs. There are some other polar compounds that technology, although in its infant stage, has the capabilities for, that we just can't touch with an HNU or any other type of real-time monitor, including the GCs, because you'll never get them past the injection ports.

JULIO REATEGUI: I agree that the coronal source is good for this application. In the example I showed, I used an ionization source that is not as good. It was a nickel-63 source. I'm sure when we try with a coronal, we can probably do better than that.

CHARLES MANN: You mentioned that using absolute peak heights wasn't effective for quantitative analysis and the improvement you got in looking at ratios. Are you intending to pursue this line? You mentioned having an extensive software development. It looks as though that might be a fruitful avenue. Do you intend to go that route?

JULIO REATEGUI: Yes. There are some things you can't patent here, so we decided to maintain some proprietary information. But my guess is that a few months down the road, the details of this technology will become more and more available.

UTILIZATION OF SHORT-TERM BIOASSESSMENTS AND BIOMONITORING AT SUPERFUND SITES

David W. Charters
U.S. Environmental Protection Agency
Environmental Response Team
Edison, New Jersey 08837

The Environmental Protection Agency's Superfund program is requiring that more extensive environmental assessments be performed at both Removal and Remedial sites in accordance with the provisions of SARA. Bioassessment and biomonitoring are presently being utilized as field screening methods at several sites to meet these conditions. The tests and studies discussed have been chosen based on their ability to be cost effective, rapid, and not delay the cleanup procedures. Field screening studies include collection of small mammals, fish, benthic invertebrates, and plants with attention paid to alterations in community structure, population dynamics, bioaccumulation of toxicants and histopathology as well as other parameters which are site specific. Laboratory tests include aqueous acute and chronic, and both elutriate and solid phase tests. Terrestrial tests include contact tests and tests for phytotoxicity. Combinations of these tests are then correlated with chemical and physical parameters collected in the field to give a more comprehensive environmental assessment of the site and its impact on the surrounding area.

Several sites will be discussed to illustrate how the bioassessments and biomonitoring are directly applied to the cleanup of sites at both the RI/FS stage and at the Removal Phase.

DISCUSSION

JAMES DELEVAN: Would you care to comment on introduced species for the purpose of a bioassay, compared to collection of indigenous species?

DAVID CHARTERS: We run both types of studies. In the case here, the lab killed all the controls, however the actual samples worked well.

Too frequently, for toxicity testing, people are very interested in running indigenous species – but it doesn't give you the needed information when running standards.

If you are dealing with an introduced species, as in taking water out and running species in that, it's a very good idea.

I'm opposed to doing exotics *in situ*. For example, if fat head minnows ever got loose in Region X there would be a lot of problems. You have to be very careful if you are introducing any exotics.

JONATHAN NYQUIST: Sometimes it takes a while for the chemicals that are released to get anywhere, as through the ground, before they hit the biosphere, so you may not see that as a stress right away. How long does the contamination have to be there before you will expect to see bioeffects?

DAVID CHARTERS: You never do any of these studies in a vacuum. In this case, you've got a site that's been there since 1949. In other cases, you've got a site that's been there since Tuesday. You have to look at the exposure routes. If the stream is impacted, it's important to know that. If it's not impacted, that's information, also.

If you ask the right questions, and you have the right data quality objectives, you will answer the question regarding the time involved. Whether contamination reaches the stream in two years or five years is a hydrogeologic question.

You can't do chemistry in a vacuum. You have to do biology in the same framework. If contamination is there, it's important to assess the environmental impact. If it is not there, that is just as important information.

JONATHAN NYQUIST: Suppose the effect is being caused by something other than the contaminants you're looking at? If acid rain, or something else is causing the problem, how do you separate that from the dump site?

DAVID CHARTERS: You separate it by using appropriate reference areas. Frequently in these cases, we do have that problem, and some people are using the same watershed as a reference.

If you're more than a kilometer from the site upstream, you're too far, assuming there are no impacts there. You want to be as close as possible to that site, and then everything is related to that reference area. There are no pristine areas left, basically.

If there is a hazardous waste site there, you've got problems. If you use the appropriate upstream controls, or general reference areas for something like small mammal collection, you can answer those questions, and it's extremely important to make sure you tie these things to that site. It doesn't do any good if you can't tie it to the site.

JONATHAN NYQUIST: If, as you suggest, you've had a site that may have been impacted since 1949 conceivably, what is the risk of using generic clumps, like piercers, grazers, and so on? These could be in a natural ratio, but the species changes would be different over long periods of time, because of acclimation and taking advantage of a situation?

DAVID CHARTERS: The difference is, in this case, we're talking hundreds of yards of stream. Nothing more. Invertebrates tend not to go upstream, they go downstream. They are the bottom of the food chain. If there are fish there, the fish are going to eat them. It's a constant turn over in population, and the population tends to work downstream.

In these particular cases, you want to take similar habitats. You want to take them close together, and you want to be very sure of where you're getting these things.

If I just took functional feeding group analysis, it does not stand alone. None of this stands alone. You need to do other things. If I give a chemist functional feeding group analysis, he won't know what to do with it. So you run multiple biological tests. You will be able to obtain what you wanted in the first place: an overwhelming preponderance of data, indicating there is an impact.

KEN HANKS: Did you look at any effects of bioconcentration through the food chain, say from the invertebrates to the fish, through the aquatic birds?

We do go up. Taking the analysis from fish to birds is a big jump, because you can't nail the birds down to that site, and if you can't do that, don't sample the bird.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPH AS A VIABLE FIELD SCREENING METHOD FOR HAZARDOUS WASTE SITE INVESTIGATIONS

Vanavan Ekambaram and James B. Burch
Senior Project and Senior Staff Scientist
Woodward-Clyde Consultants
4582 South Street Parkway, Suite 1000
Denver, Colorado 80237

Abstract

A field-operable high-performance liquid chromatograph (HPLC) was employed for the chemical analysis of water and soil at a former wood treating site. Since a gradient pump was not available, an isocratic pump was employed using a two-step elution procedure in the analysis of polynuclear aromatic hydrocarbons (PAHs), which are the primary contaminants at this site. A 50:50 mixture of acetonitrile and water was used for the low molecular weight PAHs, and a 85:15 mixture was used for the higher molecular weight PAHs. This two-step HPLC analysis provided an efficient column characteristics, similar to the commonly used gradient chromatographic systems. Good resolution ($R > 1.0$) was obtained with this system for all compounds except the benz(a)anthracene - chrysene pair. The capacity factor (k') for the column used was 2 to 16 with approximately 2500 theoretical plates. Method detection limits of 0.03 to 3.0 parts per billion was achieved for PAHs in water. The results were compared with data obtained from commercial laboratories on split samples and the comparison shows that the field HPLC provided comparable data that can be used in site characterization. Field-operable HPLC, if operated by a trained chemist, can be a viable low-cost detection and monitoring tool and can provide rapid turnaround that facilitates evaluation of remediation designs.

Introduction

Creosote, a high-temperature distillate derived from coal tar, is the most extensively used industrial wood preservative in the United States (Runker, 1). It is a complex mixture of liquid and solid aromatic hydrocarbons: 85 percent (by weight) poly nuclear aromatic hydrocarbons (PAHs), 12 percent phenolic compounds, and 3 percent heterocyclic N, S and O compounds. The abandoned and former wood treatment facilities are often sites of widespread soil and ground water contamination of the PAHs.

Certain PAH compounds are known or suspected carcinogens. The chronic toxicity of PAHs is related to the number of rings they contain; the two and three-ring PAHs are relatively non-toxic while the four and higher ring PAHs are extremely toxic. Because of their toxicity, they play an important role in the risk evaluations of ground water and soil contamination. Therefore, it is essential to obtain accurate and precise chemical data on the levels of PAHs in the environment.

PAHs are a class of compounds that are particularly suitable for analysis via HPLC. A HPLC was installed in the field laboratory at a NPL site, and was developed for the analysis of ground water at the parts per billion level. Procedures were developed so that quantitative results could be obtained on sixteen PAH compounds. The chromatographic procedure used to measure the PAH levels in ground water, and the performance criteria for the HPLC are described in this paper. The advantages of this using HPLC in the field is that it cuts down on the turnaround time and cost that are normally associated with laboratory analysis and facilitates acquisition of chemical results on several samples.

Sample Extraction

Extraction procedures for water samples can be performed by using a Sep-Pak liquid-solid extraction technique or liquid-liquid extraction. One drawback with using Sep-Pak is that it tests only a limited amount of water. Thus, samples with high levels of contamination may saturate the system resulting in poor recovery of the desired compounds. Therefore, separatory funnel liquid-liquid extraction was adopted following EPA guidelines for the analysis of PAH compounds (40 CFR, EPA Method 610, 2). This method takes advantage of the hydrophobic properties of PAH compounds (octanol/water partition coefficients of $2x10^3$ or greater) which insures a high percentage of partitioning of PAHs into the organic phase. This method also allows for larger volumes of sample to be processed (up to 2000 times in test analyses) effectively decreasing the method detection limit. Up to 1 liter of water samples were extracted with 100 ml of methylene chloride and the extract concentrated down to 0.5 ml.

HPLC Procedures

Since the column packing material is non-polar in nature, a relatively polar solvent was needed to effectively portion the sample compounds. A mix-

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ture of water and either acetonitrile or methanol are generally used in reverse phase chromatography. Acetonitrile is less viscous and more compatible with PAH compounds, and therefore, a mixture of acetonitrile and water was used as the mobile phase for both water and soil analyses. Since PAH compounds have a wide range of retention properties in chromatographic columns, a gradient pump that can change the proportions of acetonitrile and water in the mobile phase is often used in PAH analyses (40 CFR, Method 610, 2). However, since a gradient pump was not available at this site, a two-step elution procedure was adopted. A 50:50 mixture of acetonitrile and water was used for the low molecular weight PAH compounds: napthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene, anthracene, and pyrene. An 85:15 acetonitrile/ water mobile phase was used for the high molecular weight PAH compounds: (a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h) anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. PAH standards were run to determine the retention times (time from injection to elution), using the two mobile phases.

When the 50:50 acetonitrile/water mobile phase is used, the high molecular weight PAHs elute after 30 minutes, so that analysis times are extremely high and the peaks are wide. Therefore, it was necessary to change the mobile phase to 85:15 acetonitrile/water mobile phase which facilitates the faster elution of high molecular weight PAH compounds yielding shorter retention times. When the solvent system is changed, it is run through the column for at least 30 minutes before injecting a sample such that high molecular weight PAH's that may be insoluble at the head of the column are dissolved and flushed out of the column by the wash procedures. The column clean up was accomplished by several injections of 100% methanol. Several sample extracts were run with 50:50 mobile phase before the mobile phase was changed and the samples were then rerun using the 85:15 mobile phase. When 85:15 acetonitrile/water mobile phase is used, lighter PAH compounds elute in less than four minutes, but they are not resolved well enough and therefore not used for quantification. An ultraviolet absorption and a fluorescence detectors were used for measuring the signals.

HPLC Performance Results

An efficient chromatographic separation is achieved by striking a balance between resolution, speed and capacity. The analyst who wishes to optimize HPLC partitioning can alter one of these parameters only at the expense of the other two. There are several theoretical parameters, based on data collected by the analyst, which are used to evaluate the efficiency of the analytical conditions. In this discussion, the resolution (R), number of theoretical plates (N), height equivalent to theoretical plates (HETP), capacity factor (k') and method detection limits (MDL) are used to evaluate current conditions.

Resolution: Resolution is the degree to which two compounds are separated by the column. The degree of resolution between two peaks depends on the width of each peak and the distance between them. The resolution between adjacent PAH compounds analyzed by the on-site HPLC are presented in Table I. A resolution value of 0.5 or greater is generally needed to distinguish two closely resolved peaks of equal response whereas a value of 1.0 or greater should be obtained for quantifiable analyses. Table I indicates that excellent resolution values were obtained for all compounds except between benzo(a)anthracene and chrysene. The R value for these two compounds was 0.74, slightly below the cutoff for optimal resolution.

Capacity Factor: The capacity factor (k') is a measure of the column's ability to retain compounds. Small k' values indicate that sample components are poorly retained, with short retention times. Conversely, large k' values indicate that peaks will have long retention times and wide, poorly defined peaks. Studies indicate that column efficiency is optimized at k' values between 2 and 6 (Majors, 1984). But values between 1 and 15 are more practically acceptable (Johnson and Stevenson, 1978).

Capacity factors for PAH compounds in this analysis are listed in Table II. The k' values for 85:15 compounds are all within the 1-15 working range as are all 50:50 compounds except for pyrene, which has a k' value of 16.86. Although the retention time for pyrene is high (23.7 minutes), its resolution is also high (1.79).

Theoretical Plates: The concept of theoretical plates (N) is used as a measure of column efficiency. Column efficiency can be increased by increasing column length, which increases the probability that solutes will interact with the column matrix. The value of N is given by:

$$N = 5.5\ N\frac{t_r^{2}}{W_{\frac{1}{2}}}0 \qquad (1)$$

where: t_r = retention time from t=0 to the peak maximum for a given peak (minutes)
$W_{\frac{1}{2}}$ = the peak width at half the peak height (minutes).

The equation that incorporates $W_{\frac{1}{2}}$, is considered more accurate since it eliminates of peak tailing. Table II provides the capacity factors and the number of theoretical plates.

Another measure, the height equivalent to theoretical plates (HETP), allows comparison of the efficiencies of columns of different lengths.

The smaller the HETP value, the better the column efficiency. HPLC columns generally have HETP values of 0.01 - 1.0 mm. HETP values of 0.055 and 0.052 were calculated for the 85:15 and 50:50 analyses, respectively, and are in good agreement with the above range indicating good column efficiency.

Method Detection Limits: The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero

(Glasser et al., 3). (The instrumental detection limit, as opposed to method detection limit, is the minimum concentration which can be detected directly by the instrument. It does not take into account sample preparation and extraction procedures.) The spiked samples were run through the extraction and analytical procedures in exactly the same manner as other samples and the mean and standard deviation are determined for each compound. The MDL is calculated by the formula:

$$MDL = t_{(df = n-1,\ 1-\alpha = .99)} \times s. \qquad (2)$$

where: t = The students t statistic for a one-tailed test
df = Degrees of freedom
n = Number of observations
α = the probability of a Type I error
s = Standard deviation

In these calculations $df = 6$ and $t = 3.143$ (Pearson and Hartley, 1970). The MDL values for on-site HPLC analysis of PAH compounds using ultraviolet and fluorescence detectors are presented in Table III. The range of MDL's for PAH compounds is 0.16 to 3.38 µg/l. The results for the lighter PAHs were calculated using ultraviolet and for the heavier PAHs using the fluorescence detectors. These results are comparable to reported MDL's for PAH's, from EPA Method 610, which range from 0.01 to 4.0 µg/l (Cole, et al., 4). Higher MDL's are noted for 50:50 compounds (napthalene through pyrene). In practice, PAH compounds were at times reported below the method detection limits down to a concentration of approximately 0.1 ppb. The sample-specific detection limits for a given sample varied depending upon how the sample was treated (i.e., sample concentration or dilution).

Extraction Efficiency: Percent recovery ranges were established by analyzing twenty spiked samples and calculating the standard deviation(s) of the percent recoveries. One liter of reagent grade water was spiked with two milliliters of a known mixture of standard concentrations for each PAH compound. These samples were then extracted, concentrated, and analyzed according to HPLC procedures for water samples cited above. The mean percent recovery and standard deviation for each compound was then calculated. The percent recovery range was set at two standard deviations above and below the mean recovery ($X \pm 2s$). Results of these calculations suggest that good recoveries of PAHs were obtained.

Summary

The overall performance of the field HPLC procedures yielded useful results which are encouraging for future application in the evaluation of remedial actions.

Quantitative data were obtained for all PAH compounds in the µg/l range. For the off-site ground water samples, where the concentrations of PAH's are, in general, in the µg/l range, the HPLC provided quantitative information that are in reasonable agreement with the data from commercial laboratories. The calculated relative deviations were, in general, 0.5%, which could be due to differences in analytical conditions, extraction efficiencies, etc. The method blanks and method spikes analyzed via HPLC also provide results which are encouraging.

The method detection limits range from 0.03 µg/l for benzo(k)fluoranthene to 3.0 µg/l for fluorene. These values are, in general, comparable to the recommended detection limits for the EPA Method 610. Even though, one can quantify concentrations below these limits, the values would not be at a high confidence level.

The reproducibility by HPLC also appears to be well controlled. Several replicate analyses were performed on the spike samples (Table IV) and the mean (X) and standard deviations (s) indicate that the average coefficient of variation (s/X) is, in general, <30%.

In summary, HPLC offers several advantages in the hazardous waste site investigations and in the remedial designs development. Hundreds of samples can be processed at low cost and rapid turnaround time.

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TABLE I

RESOLUTION OF PAH COMPOUNDS BY ON-SITE HPLC

Adjacent Compounds	Resolution Factor (R)[1]
Naphthalene/Acenaphthalene	2.86
Acenaphthalene/Acenaphthene	4.58
Acenaphthene/Fluorene	1.38
Fluorene/Phenanthrene	2.98
Phenanthrene/Anthracene	2.50
Anthracene/Fluoranthene	3.80
Fluoranthene/Pyrene	1.77
Benzo(a)anthracene/Chrysene	0.74
Chrysene/Benzo(b)fluoranthene	3.61
Benzo(b)fluoranthene/Benzo(k)fluoranthene	1.68
Benzo(k)fluoranthene/Benzo(a)pyrene	1.53
Benzo(a)Pyrene/Dibenzo(a,h)anthracene	3.88
Dibenzo(a,h)anthracene/Benzo(g,h,i)perylene	2.23
Benzo(g,h,i)perylene/Indeno(1,2,3-cd)pyrene	1.69

TABLE II

HPLC COLUMN EVALUATION

Compound	Capacity Factor (k')	Number of Theoretical Plates (N)
50:50 Mobile Phase		
Naphthalene	3.15	2381.4
Acenaphthalene	4.17	3136.0
Acenaphthene	5.99	4096.0
Fluorene	6.63	2365.0
Phenanthrene	8.64	2818.6
Anthracene	10.66	2571.9
Fluoranthene	14.61	2820.8
Pyrene	16.86	2837.5
85:15 Mobile Phase		
Benzo(a)anthracene	2.48	1901.1
Chrysene	2.74	1656.1
Benzo(b)fluoranthene	4.24	2168.9
Benzo(k)fluoranthene	5.06	1956.8
Benzo(a)pyrene	5.94	2571.1
Dibenzo(a,h)anthracene	8.15	4213.9
Benzo(g,h,i)perylene	9.41	3832.2
Indeno(1,2,3-cd)pyrene	10.64	3620.0

TABLE III

HPLC METHOD DETECTION LIMITS

Compound	Spike Concentration (µg/L)	Mean[1] Concentration Recovered (µg/L)	Standard Deviation	Method[2] Detection Limit (µg/L)	
				HPLC	EPA 610[3]
Naphthalene	4	2.46	0.3254	1.0	1.8
Acenaphthalene (n=5)	2	1.39	0.571	1.9	2.3
Acenaphthene	4	2.92	0.8121	2.6	1.8
Fluorene (n=5)	3	2.96	0.898	3.0	0.21
Phenanthrene	2	1.71	0.2451	0.79	0.64
Anthracene	4	3.91	0.5621	1.8	0.66
Fluoranthene	4	3.60	0.4601	1.4	0.21
Pyrene	4	3.26	0.2334	0.73	0.27
Benzo(a)anthracene	4	3.49	0.1706	0.54	0.013
Chrysene	2	1.92	0.1313	0.41	0.15
Benzo(b)fluoranthene	0.1	0.087	0.0151	0.05	0.018
Benzo(k)fluoranthene	0.05	0.044	0.0095	0.03	0.017
Benzo(a)pyrene	0.1	0.086	0.0143	0.05	0.023
Dibenzo(a,h)anthracene	0.4	0.341	0.0521	0.16	0.030
Benzo(g,h,i)perylene	0.4	0.353	0.0587	0.19	0.076
Indeno(1,2,3-cd)pyrene	0.4	0.346	0.0558	0.18	0.043

[1] Number of samples analyzed = 7, except where noted otherwise.

[2] 40 CFR, EPA Method 620, 1986, NIOSH Method 5506, 1985.

DISCUSSION

GIGI BEAR: Is there any reason you are using HPLC, instead of SFC (super critical fluid chromatography) for the PAHs. In the last year, it's been proven as very efficient, very fast, and you don't have to use solvents.

VAN EKAMBARAM: These conditions were primarily set up because the HPLC was already on site. They were set up, to some degree, to do the extractions with the solvents.

RONALD MITCHUM: Did you find any chlorinated PAH's? Did you find any metabolites due to microbial degradation in the soil – like hydroxylated metabolites or methylated PAHs? Could you describe what kind of HPLC you used? And what was the detector? And could you make a comment about using a fluorescence detector here instead of, maybe, a UV detector, if that's what you used?

VAN EKAMBARAM: We did not see any chlorinated PAHs. There are several things that elute. I think those are the volatile organic compounds, and pentachlorophenol, which elutes before that. Since pentachlorophenol was one of the compounds used on site, that did not surprise us.

In fact, we also tried to change the chromatography to get quantitative data on the pentachlorophenol by changing the solvent strength a little bit, as well as some of the other compounds. But time and budget ran out, so we did not pursue that.

We also tried to institute a bioremediation program on site to degrade the PAHs, and we have been fairly successful in that. We have been injecting hydrogen peroxide, and we see fairly good degradation of the PAHs. We were able to create nontoxic zone, and two of them look like they were cleaned up. They initially showed, before the peroxide injection, about 500 ppb total PAHs. Over a period of six months we did not see any degradation. But after six months, there was a breakthrough of oxygen, and correspondingly, the PAH concentrations decreased quite a bit.

As part of this study, we wanted to use HPLC to look at the transformations we are going to make. Maybe you are cleaning up naphthalene and other PAHs that are in the ground water. But what are we producing? Are there organics which could be present in the transformation products because of these bacteria. I reviewed all the chromatograms, and they look very clean, even though there are some peaks that I could not identify because I didn't have a standard. I think by two or three months after we think it has been cleaned up, it's fairly clean. So there may be have been some transformation products, but they're all cleaned.

As to the kind of HPLC used, don't recall the exact number. We had a UV lamp on the UV detector. The fluorescence detector was an add-on item. We looked at fluorescence and UV detectors signals together. And as one would expect, the higher molecular rate PAHs had a very high cross section for fluorescence. We looked at both the UV signals and the fluorescence signal, and the correlation was pretty good. Typically, what we did on those 300 samples was to run the sample at 50, using UV-1, because for the lighter PAHs fluorescence is not that good. For the heavier PAHs, like a 85-15 mixture, we would use both the UV and fluorescence detectors. Finally, the data that we published were of the best data that we got between the different injections.

RONALD MITCHUM: The creosote area is one that is overlooked quite a bit. Still, the treatment of wood products with creosote goes on. There are some changes being made in the wood treating industry, but we still have a lot of treatment in that area. Not only sites are contaminated, but also current sites that are active. There's a process, I think, that needs some looking at.

SPECIFIC DETECTION OF ANY GAS CHROMATOGRAPHABLE ELEMENT IN SEDIMENT EXTRACTS

Michael Szelewski and Michael Wilson
Hewlett-Packard Company
Avondale, Pennsylvania 19311

Abstract

A novel microwave-induced helium plasma detector has been developed for gas chromatography. Atomic emission spectroscopy (AES) is used as the detection technique. The system can detect the component elements of any compound amenable to analysis by gas chromatography. This includes elements which have been impossible or difficult to monitor with other GC detectors.

The technique has been applied to the analysis of sediment extracts. Compound and class identification is improved compared to less specific or more tedious analysis schemes. Research has shown that elemental response may be independent of analyte molecular structure. As a screening technique, GC/AES has the ability to show the presence or absence or any gas-chromatographable element, such as chlorine, bromine, oxygen, nitrogen, phosphorus or sulfur.

Introduction

There is a wide variety of gas chromatograph detectors currently used for the analysis of hazardous wastes. One of these, the flame-ionization detector, is chosen for its universal capabilities in screening samples. Other more selective detectors, such as the electrolytic conductivity and flame-photometric detectors, are chosen for their compound specificity. This specificity is used in differentiating analytes from one another and from matrix interferences. Additionally, the sensitivity of various detectors must be considered when dealing with environmental samples.

Most recently there has been a shift in GC detector usage toward hyphenated techniques. These techniques use mass spectrometry or Fourier transform infrared spectrometry coupled to GC resulting in GC/MS and GC/FTIR respectively. GC/MS is the tool most commonly used for unequivocal identification of hazardous compounds. GC/FTIR has also been used for structural information elucidation and compound identification of hazardous wastes (1). Combining information from both GC/MS and GC/FTIR has been done to improve the number of compounds that could be positively identified in a hazardous waste site sample (2).

Presented here is a newer hyphenated technique which combines gas chromatography with atomic emission spectroscopy (GC/AES). Two recent review articles provide a thorough discussion of microwave helium induced plasma (MPD) utilized in this technnique (3,4). The detector in this work is of experimental design as shown in Figure 1 and has been previously described (5-7). The GC/AES has the ability to detect any gas chromatographable element, with a high degree of selectivity and sensitivity shown for those elements that are commonly found in hazardous waste compounds.

Work up to this point shows that GC/AES response for any element may be independent of the compound structure that contains the element. This compound independent response can yield element ratios, based on internal standards, that supplement structural information gained by GC/MS and GC/FTIR. These element ratios can be used to reduce time in spectral interpretation of unknown compounds found during hazardous waste site screening.

The combined GC/AES/Data system has similar size and weight to current field laboratory instrumentation (GC/MSD, GC/FTIR). Utility requirements (power, gases) and mobile laboratory room conditions (temperature, ventilation) are also similar.

Experimental

Gas Chromatography
HP 5890A Gas Chromatograph

Split/splitless injection port at 275°C
Split ratio = 25:1

HP 7673A Automatic Liquid Sampler
Injection volume = 1 ul

5% Phenyl methyl silicone FSCC
Initial Temp = 40°C
Initial Time = 0.5 min
Program rate = 10°C/min
Final Temp = 280°C
Final Time = 20 min

Atomic Emisssion Spectrometer
Expermental equipment utilizing a microwave induced helium plasma and movable diode array detector (5,6).

Mass Spectroscopy
HP 5970B Mass Selective Detector

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Fourier Transform Infrared
HP 5965A Infrared Detector

Sample

Sediment was gathered from a river bank within an abandoned chemical dumpsite in New York State. For a complete description of sample preparation see page 1820 of reference #1.

Results

The element specific chromatograms are shown in Figure 2a and 2b for the sediment that was analyzed. Various combinations of up to four elements can be detected simultaneously. Examples of element combinations and the corresponding emission wavelengths are listed in Table 1.

Table 1. Element Wavelength Groups

Element Groups	Emission Wavelenght (nm)
Carbon	247.9 (2nd order)
Hydrogen	486.1
Chlorine	479.5
Bromine	478.6
Carbon	193.1
Nitrogen	174.2
Sulfur	180.7
Fluorine	685.6
Oxygen	777.2

Having element specific chromatograms gives excellent information about unknown samples. Figure 3 shows the content of nine elements in the compounds in the dump site soil extract that have been separated by gas chromatography and detected by atomic emission spectroscopy.

For screening purposes the presence of gas chromatographable compounds that contain specific elements can readily be determined. There exists the possibility for interference in element detection from another element present in large quantities, such as carbon.

Element selectivities and sensitivities are shown in Table 2. Also included are sensitivities for other common GC detectors. The AES detector compares favorably with these GC detectors while combining the specificity of more than one of these.

During remediation of a hazardous waste site, where contaminant levels should be decreasing, the GC-AES can be used to detect low levels of these contaminants. Additionally qualitative information on the compounds of interest and any new ones that may appear can readily be obtained from the element specific chromatograms.

A second area in which the GC/AES can contribute in the screening process is that of site characterization. A commonly accepted technique for compound identification is GC/MS. For target compound analysis automated library search and quantitation work well. For non-target compound analysis, however, GC/MS can present problems. Detected analytes may not be present in on-line search libraries or the quality of the library match may be too low to positively identify the compound. Other hyphenated techniques such as GC/FTIR can provide additional structural information for unknowns in environmental samples (2). There still exists the possibility for disagreement between GC/MS and GC/FTIR library searches for the aforementioned reasons.

Table 2. Typical GC/AES Results with Comparison to Other GC Detectors

	GC Detectors			AES Detector	
	Select	MDL	Atom	Select	MDL
FID		5	C		0.5
TCD		1000	C		0.5
			H		1
NPD	35K	0.5	N	25K	15
	70K	0.1	P	50K	1
ECD	1-100K	0.02	Cl	25K	15
			Br	10K	15
FPD	10K	2	S	10K	2
		0.5	P	50K	1
ELCD	100K	1	Cl	25K	15

Select. = relative to C
MDL = pg/sec of element

Manual interpretation of the spectra can be time consuming. The GC/AES can speed up the interpretation process by providing the analyst with:

1) information on the specific elements that are present or absent, and

2) approximate ratios of the elements based on an internal standards.

Figure 4a illustrates chromatograms from all three spectral detection techniques. The carbon and chlorine specific shromatograms from atomic emission of Figure 4b are used in the following discussion in comparing information from MS, FTIR and AE.

As an example, Peak #1 was identified by GC/MS and GC/FTIR to be o-chlorotoluene. Known internal standards could have been added to the extract prior to GC/AES analyses of course, but this peak had already been identified. Peak #2 was not detected by GC/FTIR. The GC/AES data gave a C:Cl ratio of 1:0.29 which supports the second best match in the GC/MS library search. Oxygen was not present which eliminated the possibility of the best library match by GC/MS.

In previous work$^{(2)}$, peak #3 had been tentatively identified as an alkane. GC/AES showed the presence of chlorine and the lack of other heteroatoms such as O,F,N, S or Br. The C:Cl ratio of 1:0.1 supports the best GC/MS library match found when the sample was used with the HP 5970B in the current work.

Conclusions

The GC/AES has the following advantages and benefits over current GC detectors for hazardous waste site characterization and monitoring.

1) Element specific detection
    - potential time savings in sample preparation

2) Multiple element detection
    - reduces space needed at on-site monitoring laboratories by limiting number of GCs needed with multiple detectors

3) Compound independency for response factors
    - saves time by reducing the number of standards that have to be analyzed

4) Provides element ratios
    - reduces time for interpetation of GC/MS and GC/FTIR data for non-target compounds

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(7) Wylie, P.L., Quimby, B.D. and Sullivan J.J. "Application of an Experimental Microwave-Induced Helium Plasma Detector for Gas Chromatography", R.M. Barnes, Ed., **Proceedings 1988 Winter Conference on Plasma Spectrochemistry**, San Diego, January 1988, p 181.

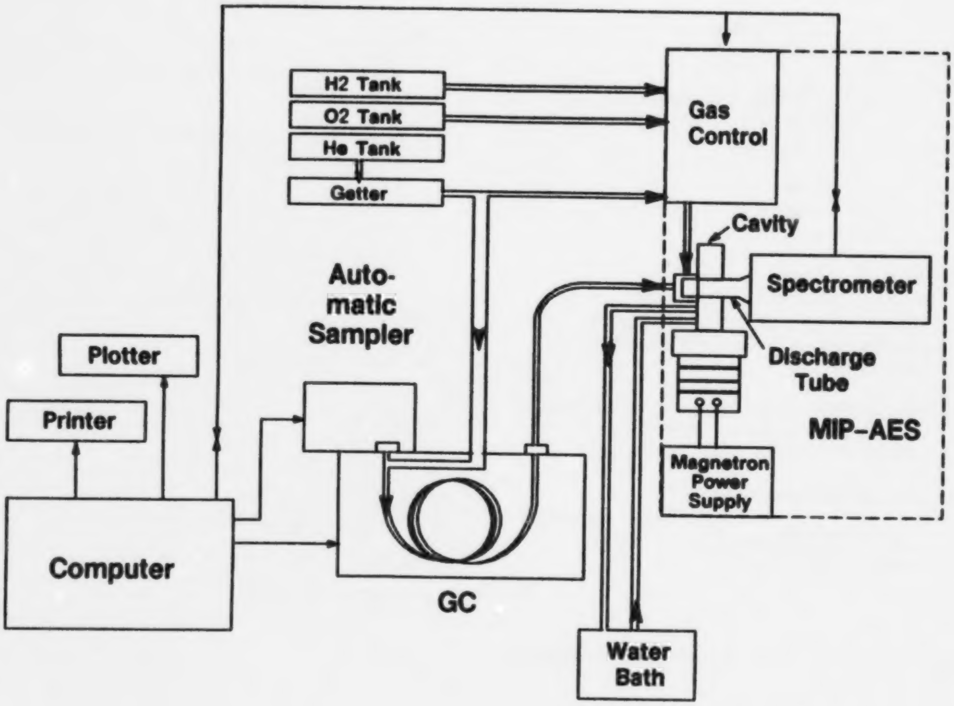
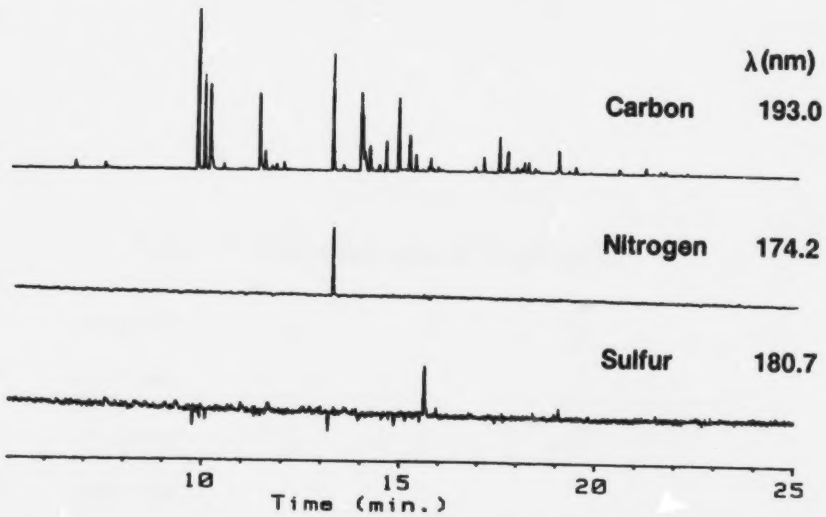

H2 Tank
O2 Tank
He Tank
Getter
Gas Control
Cavity
Spectrometer
Auto-matic Sampler
Discharge Tube
Plotter
Printer
MIP–AES
Magnetron Power Supply
Computer
GC
Water Bath

Figure 1. Diagram of Experimental GC/AES System

Chemical Dump Site Soil Extract

2a Carbon, Nitrogen, Sulfur Screen



2b Carbon, Chlorine Screen

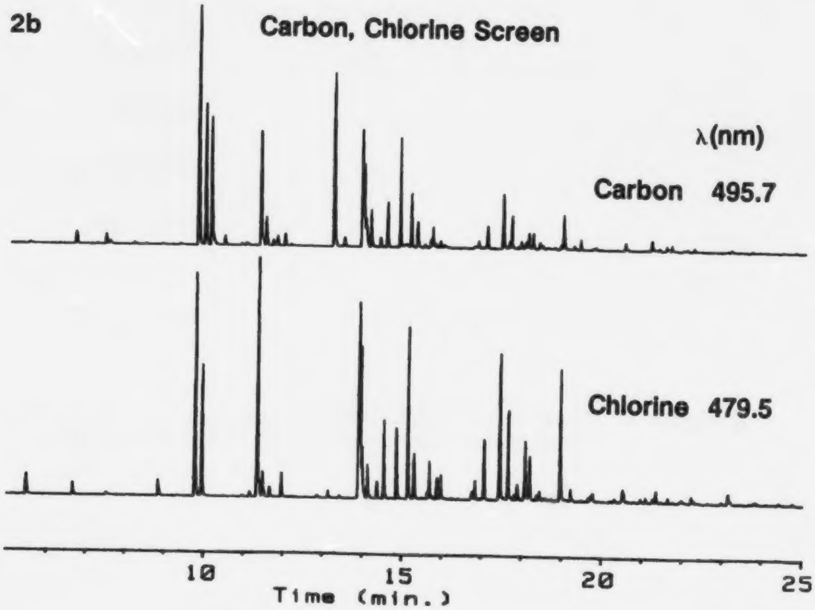
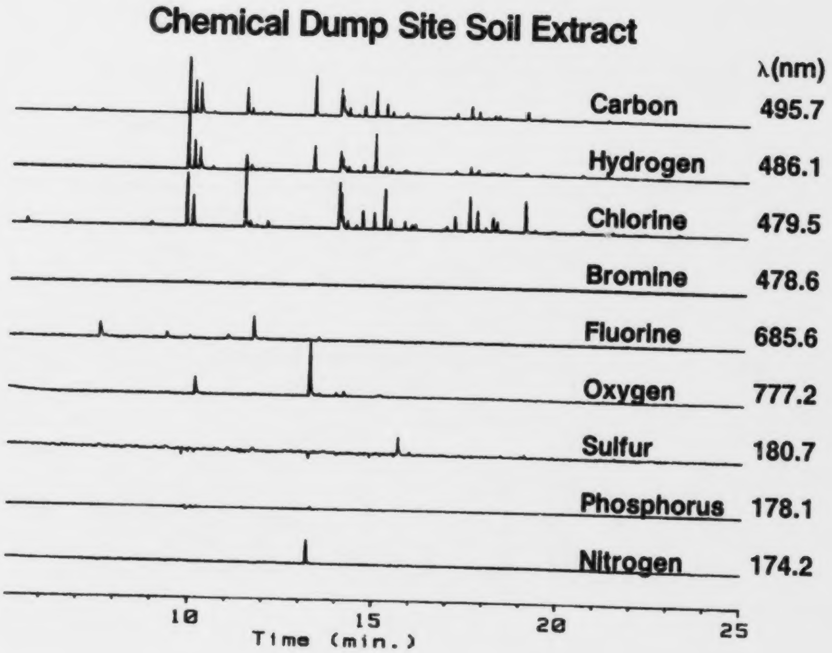


Figure 2. Examples of Screening Chromatograms



Chemical Dump Site Soil Extract

Figure 3. Nine Element-Specific Chromatograms from GC Analysis of Chemical Dump Site Soil Extracts

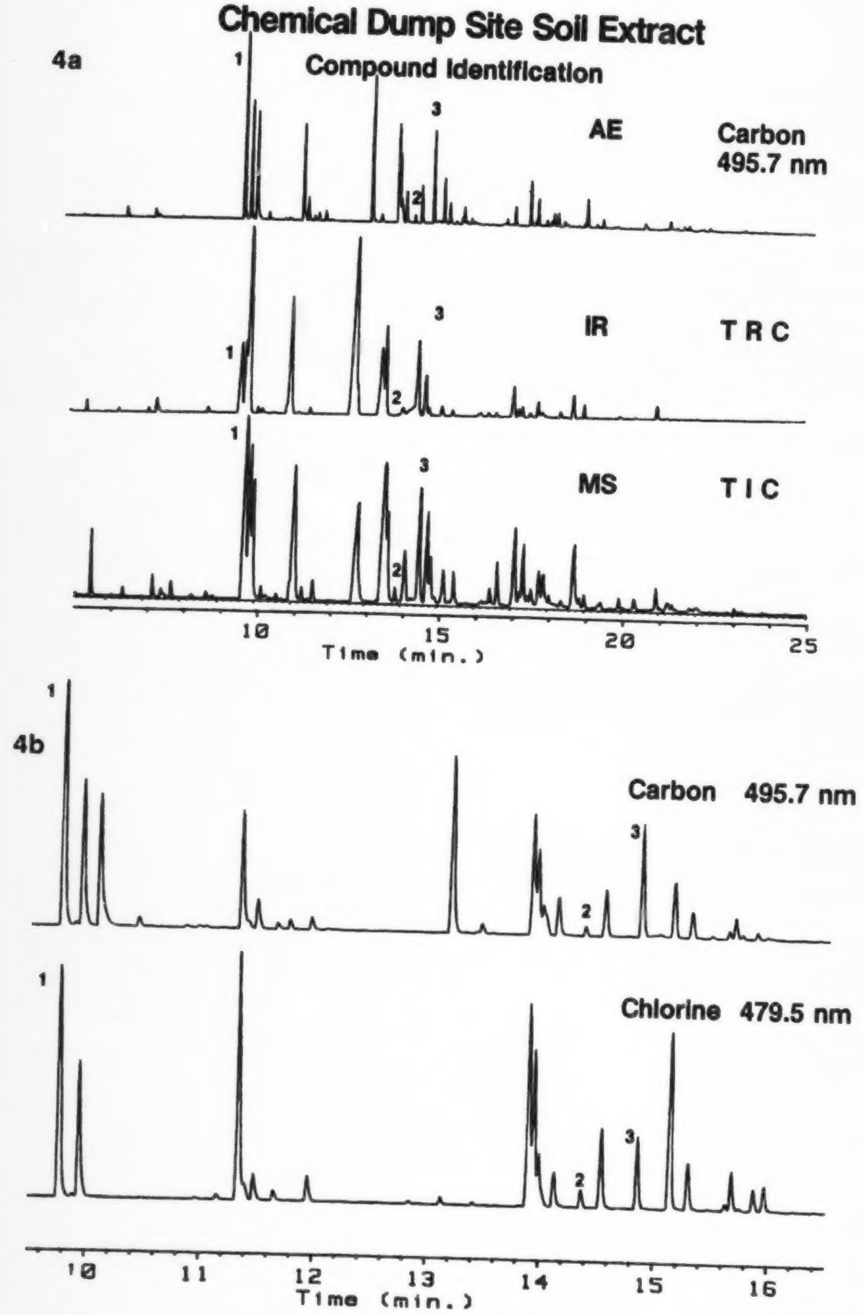


Figure 4. Chromatograms from GC/AE, GC/MS and GC/IR

DISCUSSION

JOHN EVANS: I was curious about the 40 to 1 split. It's fairly high. Why you did not discuss the hydrogen results and your ratios?

MICHAEL SZELEWSKI: The split was run primarily because of the high concentration of the extract, and not wanting to dilute it down too many times and subject it to potential contamination with other things. The extract is so highly concentrated that without running it split on the atomic emission detector, we would be outside the linear range on the carbon channel. The only reason I didn't show the hydrogen channel is that it looks very similar to the carbon channel.

JOHN EVANS: You must have a ratio of some sort. You were just showing partial formula. And that's all. Why didn't you ratio the hydrogen?

MICHAEL SZELEWSKI: No particular reason. The hydrogen ratios on these particular compounds so work out fairly well.

ED HEITHMAR: I notice that for things like bromine, you only have a linear dynamic range of about 1,000. Is that due to self absorption or to energy-limiting factors in the plasma?

MICHAEL SZELEWSKI; I don't really know. I don't think it's due to energy levels in the plasma. I think there are interactions inside the plasma within the walls of the tube in the cavity. That has been the biggest limiting factor up to this point. Getting the proper combination of "secret sauces" and reagent and make-up gases has been the single biggest thing that has improved dynamic range.

ED HEITHMAR: So with high concentrations, you don't see a great deal of plasma poisoning for coeluting compounds – hydrocarbons on top of something else.

MICHAEL SZELEWSKI: No.

UNIDENTIFIED PARTICIPANT: One of the problems that I've always noticed is that your ability to run heteroatoms is great. Our ability to get heteroatoms to the GC is not so great. Unfortunately, a lot of sulfur-containing compounds and phosphorus-containing compounds chromatograph very well. Can you comment about the future of HPLC interfaced to this thing?

MICHAEL SZELEWSKI: At this point, it's not even available in the GC version. As far as HPLC on the priority list of things to look at, it is there. It is the next obvious choice, but there is no direct research going on right now. I would say that it's probably number one on the list of things to do next, as far as this specific detector is concerned.

THE U.S. EPA FIELD ANALYTICAL SCREENING PROJECT (FASP)

G. Hunt Chapman
Ecology and Environment, Inc.
Arlington, Virginia

Scott Fredericks
Hazardous Site Evaluation Division
U.S. Environmental Protection Agency
Washington, D.C.

ABSTRACT

In response to the concerns raised by Congress and the public, the U.S. Environmental Protection Agency (U.S. EPA) is evaluating means of improving charaterization of hazardous waste sites through enhancing on-site analytical capabilities for the investigation of hazardous waste sites. The Field Analytical Screening Project (FASP) has been established in an effort to address these concerns. FASP will be used to generate quick turnaround screening data where the rigorously qualified CLP data is not required. It is designed to provide screening data for specific compounds known to be on the site from previous CLP data. FASP will be used mainly during Listing Site Inspections (LSIs) to help determine the extent of contamination and in choosing samples to document a contaminant release for the Hazard Ranking System (HRS).

A Base Support Facility (BSF) is located in each region to serve as a staging area for all field activities. A support vehicle is equipped to perform screening for target compounds at the site. Instrumentation will be stored at the base support facility and transferred to the support vehicle as needed for specific sites.

INTRODUCTION

Changes in the pre-remedial process since the enactment of SARA have increased the need for on-site screening. The development and implementation of a national field screening program depends on a framework that provides a consistent approach to produce data of a known quality. However, this framework must be flexible enough to meet specific regional needs. The FASP approach described in this paper provides a structure that meets this dual requirement.

THE FASP PROGRAM

The FASP Approach and Structure

U.S. EPA goals have been used to develop a FASP concept paper which is used to define the approach, structure, and role, as well as to assist in the implementation of FASP. In the concept paper, FASP Data Quality Objectives (DQOs) define the levels of data quality required for specific tasks performed during a site inspection. These tasks are discussed later in this paper.

A FASP working group has been established to develop and expedite FASP. It consists of knowledgeable and experienced U.S. EPA and contractor personnel from each region. These include the National FASP project manager and the Zone I and II Screening Managers (ZSMs) to coordinate and implement the national management plan, and Regional Screening Coordinators (RSCs) from each region to implement regional programs. The RSCs have conducted regional feasibility studies to determine detailed plans and assist final decisions regarding the level and type of field screening to be undertaken in each region. This process began by asking regional data users what quality of data they needed for specific pre-remedial tasks. Defining this level of data quality facilitated the determination of the appropriate levels of instrumentation, and the regional approach and application of field screening.

A national FASP framework is necessary to provide the consistency and coordination needed to support U.S. EPA pre-remedial goals. This structure is a very important aspect of the FASP concept. It is managed through centralized organization and coordination by the Zone Screening Managers (ZSM) and the FASP working group. All aspects of FASP are scrutinized and discussed by working-group members to insure that the over-all project goals are met and that they are standardized for all regions. The nationally coordinated FASP program includes the following:

Analytical methods - consistency of the methodology is extremely important. The use of standardized methods insure a consistent capability and a predictable level of data as defined by the DQOs. A FASP methods manual containing approved analytical methods is distributed to each region.

QA/QC protocols - A FASP QA/QC manual is provided to each region detailing a comprehensive QA/QC protocol. It includes proper calibration techniques, use of matrix spikes and duplicates, personnel training, documentation procedures, maintenance schedules, use of analytical-grade reagents, etc.

Safety procedures - A FASP safety manual is issued to all regions. This includes safety protocols to be followed during all FASP activity.

Personnel training - A training program is established in conjunction with the appropriate product vendors as well as with experienced FIT chemists. A FASP training center is established where FIT chemists can receive additional hands-on training if needed.

Analytical instrumentation - national coordination of instrumentation purchases ensures that FASP goals are met. This does not mean that all regions must use the same instrumentation.

Data Quality Objectives (DQOs) - FASP DQOs are used to define the data quality required for specific on-site tasks. They are to ensure that specific, consistent standards are maintained for on-site screening during various pre-remedial activities in all U.S. EPA regions.

All of these aspects of the centrally managed FASP project are essential in providing consistent, reliable data that can be used with confidence by the U.S. EPA in all regions.

In general, the FASP emphasis is the screening of target compounds known to be onsite from previous sample analysis. This screening data is used to complement CLP data as required by data users. This approach allows for customized screening of only the compounds of interest, which shortens the time required for screening. Customized screening methods are developed for many organic compounds on U.S. EPA's Target Compound List (TCL). Methods and QA/QC protocols are defined for all FASP screening to provide a defined data quality that meets established DQOs. FASP is presently implemented in six "pilot-study" regions. If the pilot studies prove to be beneficial, FASP will be implemental in the remaining U.S. EPA regions.

The Role of FASP

FASP is intended to support site investigation activities during a Screening Site Inspection (SSI) or a Listing Site Inspection (LSI) where target compounds are identified from prior analysis. Samples are screened specifically for these target compounds and the methods are optimized for them. FASP is not well suited to screen for a broad range of unknown contaminants. Uncharacterized sites and unknown contaminants require the usual CLP analysis which includes mass spectral confirmation for organic compounds and Inductively Coupled Argon Plasma (ICAP) for metals. FASP is best utilized on large sites that require screening a small number of contaminants in many samples. As mentioned above, the screening methods are customized for these target compounds, which allows for rapid screening at a lower cost. In some cases, the use of specific instrumentation to optimize screening methods for target compounds allows for detection limits below Routine Analytical Services (RAS) CLP results. A portion of the FASP samples can be split and sent to the CLP for confirmation.

FASP can provide several important benefits to the inspection team on the site. One of the most important of these is on-site feedback. In the past, Field Investigation Teams (FITs) had to rely on visual inspection or intuition to choose sampling points during inspections. This has often resulted in insufficient site characterization or the analysis of inappropriate samples and return trips to the site for resampling. On-site feedback of FASP screening results can aid the FIT in site characterization. This includes finding "hot spots" on site and determining the extent of contamination. This is especially useful at large sites where an equal number of CLP samples would otherwise be cost prohibitive. Once the FASP data is reported, the FIT team can reliably determine the appropriate samples to be sent to the CLP for confirmation. These CLP samples are then used for litigation purposes or other uses requiring more rigorous protocols.

On-site feedback is also used to direct on-going work, redirect sampling efforts and modify work plans. This includes the installation of monitoring wells where screening data can determine the depth of well screen placement. Another application is in removal operations where screening data can determine if enough contaminated material has been removed while the removal equipment is still on site. When FASP results indicate that enough material has been removed, a sample sent to the CLP can be used for confirmation.

Another benefit of on-site screening is the optimization of air monitoring programs. Air monitoring for volatile organic compounds is performed with composite samples using absorbant tubes such as Tenax, or with grab samples using Tedlar bags or some other suitable container. When using Tenax, the time between sampling and analysis must be minimized. This is because Tenax is such a strong adsorbant, it can become contaminated while in storage. Other factors such as artifact formation and break-through often complicate and/or invalidate the results. In addition, grab samples taken on site have very short holding times and must be analyzed on site. Therefore, it is best to perform air monitoring on site where holding times are minimized and sampling problems can be corrected while the samplers are still there.

Soil-gas sampling for organic contaminants is a technique that can best be used in conjunction with field screening. It is a technique used primarily to delineate the horizontal profile of volatile organic groundwater contaminant plumes. It improves the placement of monitoring wells used to document groundwater contamination. The soil-gas sample can either be a composite sample

(Tenax or other adsorbant) or a grab sample. These samples should also be analyzed on the site for the same reasons discussed for air samples.

FASP Implementation

FASP has been implemented through a phased approach, i.e. building blocks. Each phase represents a specific TCL fraction or group of compounds. The phased approach is used to allow regions to select analytical capabilities based on their particular requirements. Each phase's implementation includes instrumentation, screening methods, training, and QA/QC protocols. This comprehensive approach ensures that all FASP results meet the required level of data quality established in the DQOs. Each phase establishes specific capabilities and builds on the previous phase. The phased approach addresses the need to implement a basic field screening capability while ensuring that steps are taken to administer the program properly, thereby meeting the goals of proper training, documentation, and instrumentation.

Phase 1 involves screening for volatile organics in water, soil, and grab air samples. The water and soil samples are screened using a portable Photovac gas chromatograph (GC) using the head-space technique. The air samples are screened directly from the Tedlar bag using the Photovac. The Photovac GC was chosen for Phase 1 because it is portable and can obtain very low detection limits for many TCL compounds. The portability is needed so that FIT chemists can easily go to the field with minimum support. A field kit was fabricated by the FIT to support the Photovac in the field. It contains all necessary support equipment needed to screen samples on site. This approach for Phase 1 allows for the quickest and easiest implementation of a field screening capability while the FASP support facilities are being procured and/or constructed.

The Base Support Facility (BSF) is also part of Phase 1. This is used as a staging area for all field screening activity. It is used for calibration and maintenance of instrumentation, storage of supplies, method development, and to screen samples from smaller sites (with fewer samples) when mobilization of the support vehicle is cost prohibitive.

Phase 2 involves screening for PCBs in water and soil. This phase involves the use of compact transportable GCs and equipment required to perform basic sample preparation and extraction. PCB analysis requires more sophisticated equipment and sample preparation facilities such as utilities, shelter, and adequate working space. This requirement is the justification for the procurement of the support vehicle which is part of Phase 2. This support vehicle is also required for all field screening performed in subsequent phases.

The support vehicle is equipped to handle simplified sample preparation and/or extraction as well as the space needed for several small GCs. Because of the limited space in the support vehicle and the customized screening at each site, the support vehicle will be equipped with only the instruments and equipment needed for the target compounds at that site. The Base Support Facility is used to keep all instruments and other equipment in "field-ready" condition when needed. When the Support Vehicle is not in the field, it will be parked next to the Base Support Facility to increase the total lab working space and allow for rapid outfitting for the field.

The remaining phases are:

- o Phase 3 - Screening for chlorinated pesticides in water and soil.
- o Phase 4 - Screening for selected base/neutral organics in water and soil.
- o Phase 5 - Screening for selected acid-fraction organics in water and soil.
- o Phase 6 - Screening for selected metals in water and soil.
- o Phase 7 - Special screening, i.e. composite air sampling, GC/MSD, herbicides, Purge and Trap, etc.

Phases 2-5 all use similar types of transportable, compact GCs equipped with different columns and specialized detectors.

Phase 6 can use one of two methods for metals analysis. First, Atomic Absorption Spectrophotometry (AAS) is the method more similar to CLP methods. However, there are several disadvantages for field screening. The samples must be acid digested to get acceptable results for most samples. This can be both dangerous and time consuming in the confined space of the Support Vehicle. Also, only one metal can be screened at a time. The biggest advantage of AAS is that the method detection limits are comparable to CLP. The second choice is X-Ray Fluorescence (XRF) Spectrophotometry. This method does not require acid digestions and most TCL metals can be screened simultaneously. Its disadvantages are that the detection limits are very high and that matrix corrections are often required for an accurate result. This can be a problem when screening differing and unknown environmental matrices.

CONCLUSION

In conclusion, it should be noted that the capabilities of sample screening and laboratory analysis in general are governed by instrumental sophistication and capabilities. As FASP continues and instrumentation develops further, the quality of screening data will also improve.

The importance and benefits of on-site feedback and matching of the screening methods to site DQOs cannot be overstated. Proper management and implementation of FASP can greatly benefit the entire pre-remedial program in terms of efficiency, cost savings and time savings.

CONCLUDING REMARKS

LLEWELLYN WILIAMS

These past three days you have been exposed to a fairly broad range of technologies; perhaps some of you were surprised with the diversity. I think you may also have been surprised that some of these technologies are as far along as they are, that they are out there, and data are being produced with them.

Some of you were also probably surprised that some of the technologies we have heard about for years are not quite where we thought they were, and that some of them are going to require new developments and breakthroughs in materials and our approaches, before they can become true monitoring, or measurement tools that we can use in the field.

What was important was to bring this kind of group together in one place. We have a balance of academics, we have the people from the private sector, from commercial operations. We certainly have a good representation from the Federal sector and States, as well.

It's important that we know where this technology is. Don't be disappointed that it isn't where we hoped it would be. Let us know where it is, so that we can do our planning accordingly. This is very important for all of us, certainly for us as regulators.

We saw some opportunities to perhaps save money in the way we do our operations in the future. Cost savings are great, but not if they are at the expense of the environment or human health and safety. We need good quality assurance to be associated with our field methods. We need good data quality objectives. We need to know what kind of data we must have to make critical decisions.

Also, we may want to think about taking those cost savings and turning them back into better monitoring and better measurement. Rather than think only in terms of saving money, let's get more confidence in the decisions that we make, upon which our environmental and human health and safety depend.

We have seen opportunities to perhaps avoid some of the high cost of environmental zeros, using lower-cost technologies that enable us to key on those samples that are more appropriately taken to a laboratory for high tech analysis.

We know of programs in the past that could have saved hundreds of thousands of dollars if they had a screening method available to them — where the high cost of conventional methodology ran us into the ground.

Some of these operational hurdles will be overcome. But it takes time to see these technologies develop, and to see the changes. And since some breakthroughs are necessary in some of the technologies, it will take time.

We are in a position in many cases to be able to help. Can we do it all, do we have the kind of bucks to support everybody's activity? No. We need to be looking for those kinds of technologies that are going to help us do our job in the near term, but with an eye toward those special high-potential technologies that are going to help us all in the future.

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QUALITY ASSURANCE PLAN USED AT THE LOVE CANAL EMERGENCY DECLARATION AREA INDOOR AIR ANALYSES BY THE TAGA 6000E MASS SPECTROMETER/ MASS SPECTROMETER

Thomas H. Pritchett
U. S. EPA Environmental Response Team
Edison, New Jersey

David B. Mickunas & Nicholas Kurlick
International Technology Inc. (REAC)
Edison, New Jersey

ABSTRACT

A quality assurance/quality control (QA/QC) plan was developed for a Trace Atmospheric Gas Analyzer (TAGA) used in monitoring indicator chemicals in ambient air during the Love Canal Emergency Declaration Area habitability study. The QA/QC requirements were instituted to assure the data would be technically sound and legally defensible.

Eight data quality objectives were defined for the study (Table I). Six of these objectives related directly to the instrument's performance, which set criteria for accuracy, precision, detection limits, sensitivity decay, and sampling efficiency. The remaining objectives were concerned with the comprehensiveness of documentation and sampling.

INTRODUCTION

In the Autumn of 1986, the US EPA Region II requested the assistance US EPA Emergency Response Team (ERT) by making the TAGA 6000E Mass Spectrometer/Mass Spectrometer (MS/MS) available during the indoor air analyses for the Love Canal Emergency Declaration Area (EDA) Habitability Study. As one of three environmental studies cited in the "Love Canal Emergency Declaration Area Proposed Habitability Criteria"[1], the purpose of this study was to report the results of the air assessment for indicator chemicals. These results, together with the other environmental studies, are intended to provide data to assist the New York Commissioner of Health in determining the habitability of the structures within the Emergency Declaration Area.

The air assessment study was designed to monitor residential structures in the EDA for chemicals whose presence in indoor air would strongly suggest that they originate from the Love Canal. Two compounds and their structural isomers, referred to as the Love Canal Indicator Chemicals (LCICs), were chlorobenzene and chlorotoluene. The EDA sampling strategy included seasonal variations, diurnal variations, rainfall and groundwater levels, occupied versus unoccupied status, and sampling randomness. Furthermore, the sampling strategy asserted that the presence of any LCIC in the indoor air of a residence is adequate indication that the habitability of the residence requires further evaluation. The latter was the recommendation of the Technical Review Committee (TRC), which is composed of representatives from state and federal agencies involved with the Love Canal. This requirement was a result of the "Pilot Study for the Love Canal EDA Habitability Study"[2] conducted in 1986 where the number of detections was too limited for statistical analysis and, therefore, would require an excessive number of controls to be sampled. Consequently, the TRC made the decision to sample each physically-sound, residential structure in the EDA, assuming permission could be obtained from the people living in these structures, in lieu of using a control population.

PROCEDURE

Appendix A of the "Love Canal Full-Scale Air Sampling Study Quality Assurance Project Plan"[3] contained a detailed discussion of the standard operating and reporting procedures used by the TAGA group during the study. Those operational procedures directly related to the TAGA quality assurance plan are:

1) Initial Tuning - At the start of each analysis period, the instrument was readied.

2) Instrument Calibration - At the start of each analysis period, before each residential sampling, and prior to final QA/QC analyses, the TAGA was calibrated by using the LCICs.

3) Measurement of Sampling Line's Transport Efficiencies - At the start and end of each analysis period, but after the instrument was tuned and calibrated, the transport efficiencies of the sampling line for the LCICs were determined.

4) QA/QC Sample Analyses - At the start and end of each analysis period and during external audits, QA/QC sample were analyzed to measure the accuracy, precision, or detection limit and quantitation limit verification.

5) Sample Air Flow (SAF) Transducer and Mass Flow Controller (MFC) Calibration - At the start and after the end of each sampling phase,

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every week during a phase, and after repairs, the SAF transducer and the MFC were calibrated using an NBS traceable standard.

RESULTS AND DISCUSSION

Overall project management coordination was the responsibility of CH2M Hill, Inc., the Love Canal remedial contractor, under the direction of the US EPA Region II. CH2M Hill responsibilities included designing the overall sampling program, generating the overall Quality Assurance Project Plan (QAPP), and coordinating of sampling process and its review. The ERT assumed responsibility for developing the TAGA analytical methodologies and for developing the quality assurance plan for the TAGA-generated data. Northrop Services, the operations contractor for the Quality Assurance Branch of the EPA's Environmental Measurements Support Laboratory at Research Triangle Park, NC (EMSL/RTP), assumed responsibility for providing external field QA audits and TAGA performance evaluation (PE) samples during all phases of the study. The TRC had final approval authority over all phases of the sampling program, including the TAGA quality assurance plan.

The design and data quality objectives (DQOs) of this project received intense examination. The QAPP, which incorporates the TAGA Standard Operating and Reporting Plan (SORP) and the sampling program, was not approved until it was thoroughly reviewed by all agencies represented on the TRC and by the Quality Assurance Branch of EMSL/RTP. The DQOs were instituted to assure data acquired would be technically sound and legally defensible. These goals were achieved by:

1) ensuring that the required sensitivity was met;
2) ensuring that the required precision and accuracy were met;
3) ensuring that the response factor drift was within specifications;
4) ensuring that the ancillary equipment was functioning properly;
5) ensuring that the data was reviewed in accordance with the QAPP; and
6) ensuring that the sampling was complete.

Associated with the DQOs were one of the three, following levels of action. These levels were:

1) R - Requires sampling or resampling of a residence;
2) A - Requires correction of problem before sampling can continue; and
3) G - Requires additional PE analyses, but sampling can continue.

The "R" criteria were applied to the sampling and documentation completeness. The "A" criteria were applied to instrument and ancillary equipment performances involved with the analyses (with the exception of the accuracy data quality objective). The "G" criteria were applied to the accuracy DQO (due to the experimental nature of certification of PE Summa canisters).

The accuracy DQO was modified for the initial segments of the study. Due to problems with certification, no data was available for Phases 1 and 2 for the 6-liter Summas or for Phase 1 for the 16-liter Summas. However, a Scott gas cylinder, other than the one used for calibration, was analyzed as an internal check. The measured error exceeded 25% only once in the program and on that day, three separate accuracy checks were performed with two within tolerance. The verification of detection and quantitation limits by spiking the sample 1 ppb and 2 ppb, respectively, above their limits never failed. Furthermore, the Northrop Services provided for each phase external audit Summa canisters to assure the required accuracy condition was met. The analyses of these canisters by the TAGA always had the mandatory accuracy.

The precision data quality objective required that, within a phase, standard deviation from the mean be less than 25%. In all cases this objective was met.

The results of the detection limit data quality objective are summarized in Table II. This specification demands that the detection limit be less than 4 ppb for both LCICs. All of the reported LCIC detection limits met this criteria when rounded to the closest whole number. Only one detection limit, 4.2 ppb, for one of the LCICs was greater than 4.0 ppb. Even though this detection limit satisfied the DQO when rounded down, the house involved was resampled during that phase as a within-phase replicate house analysis. Additionally, it was chosen as one of the houses that was analyzed during each of the remaining phases as an overlay analysis The four additional sets of detection limit data met the detection limit specification.

The data quality objective requiring that average response factor decay percent between consecutive calibrations for both LCICs be less than or equal to 15% was exceeded several times for one or both LCICs during the study. In all cases the appropriate corrective action was taken and the sensitivity stabilized. Additionally, in all cases the response factors acquired after the excessive decay were sufficient to give the TAGA the required sensitivity to continue operations. The calibration system is diagrammed in Figure 1.

The accuracy of the TAGA calibrations, as determined by the accuracy of the flow rate measuring devices, was a data quality objective. Two different flow measurements were used in calculating the LCIC calibration concentrations. The mass flow controller (MFC) measured the flow rate of the calibration gas and the sample air flow (SAF) measured the flow rate of the ambient air dilution stream. The specification for the accuracy for all of the SAF and MFC calibration points mandated that the error be less than or equal to 10%. Additionally, during each phase the Northrop Services conducted an audit of both the SAF and MFC measuring devices using an NBS traceable laminar element to check their accuracy. All SAF and MFC calibration points audited for all phases of the study had an error less than 10%.

The data quality objective requiring that the total loss of LCICs in the sampling line be less than or equal to 15% translated into a transport efficiency percentage of greater than 85%. The equipment for determining transport efficiency is diagrammed in Figure 2. All percent transport efficiencies for all phases of the study were greater than 85% for both LCICs. During the first phase a heated transfer line was used to maintain the line temperature greater than or equal to 70°F. This was done in an effort to prevent losses of LCICs by condensation. An experiment conducted between the first and second phases demonstrated that an unheated Teflon line could transport the LCICs at temperatures as low as 32°F. An unheated transfer line was used for the duration of the study. Additionally, the ambient air temperature was monitored for each transport efficiency test. The lowest temperature observed was 31°F. The results of the transport efficiencies for Phases 2-4 are plotted vs. temperature in Figure 3.

Sampling 100 percent of the EDA structures for which permission to gain entry was granted and for which the structures was determined safe to enter was a data quality objective. CH2M Hill was responsible to assure this DQO was met. During the course of this study, 562 EDA residential structures were sampled.

The DQO requiring that the documentation be complete and consistent for sampled residences was met. Acceptable data packages were generated for all residences sampled by the TAGA. The consistency and completeness of the data packages were checked by two different groups, internal and external review teams, under the direction of the ERT QA/QC coordinator. All of the data packages generated during this study passed these two reviews and all significant inconsistencies or omissions were corrected.

The internal data review group was responsible for ensuring that the documentation package was complete, all data entries were consistent for the documentation package, and all data entry errors were corrected. The external data review group was responsible examining the documentation package for the completeness and consistency and documenting on a comment log sheet to the ERT QA/QC coordinator any anomalies. The ERT QA/QC coordinator was responsible for reviewing the comments by the external data review group and categorizing the discrepancy as:

1) the anomaly does not affect the data quality - no action required;
2) the anomaly does affect the data quality - action by the data review group is required;
3) the anomaly does affect the data quality - action by the ERT QA/QC coordinator is required; or
4) the anomaly does affect the data quality - the house must be resampled.

CONCLUSIONS

Technically sound and legally defensible data can be acquired with the TAGA technology if the proper QA/QC protocol is invoked. The QA/QC protocol had redundancies to ensure anomalies in the data did not corrupt the quality.

REFERENCES

1. "Love Canal Emergency Declaration Area; Proposed Habitability Criteria," New York State Department of Health, Albany, NY, 1986.
2. "Pilot Study for the Love Canal EDA Habitability Study," CH2M Hill Southeast, Inc., Reston, VA 1986.
3. "Love Canal Full-Scale Air Sampling Study Quality Assurance Project Plan," CH2M Hill Southeast, Inc., Reston, VA 1987.

TABLE I. TAGA Data Quality Objectives for the Love Canal EDA Air Habitability Study.

Objective	Criteria	Criteria Key
1. Overall TAGA Accuracy as Determined by Performance Evaluation Analyses (% error of reported concentration)	≤25%	G
2. Overall TAGA Precision within a Phase by Periodic Analyses of Same Cylinder (% error of reported concentration)	≤25%	A
3. Detection Limits for LCICs (ppb)	≤4	A
4. Allowable Decay Between Consecutive	≤15%	A
5. Accuracy of TAGA Calibration (% difference, reported vs. actual)		
Sample Air Flow	≤10%	A
Mass Flow Controller	≤10%	A
6. Total Loss of LCIC in Sampling Line (% loss of ion signal)	≤15%	A
7. Residential Structures Sampled (% of EDA structures for which permission to gain entry was granted and for which the structure was determined safe to enter)	100	R
8. Documentation Complete and Consistent for Sampled Residences (% complete)	100	R

1) R - Requires sampling or resampling of a residence;
2) A - Requires correction of problem before sampling can continue; and
3) G - Requires additional PE analyses, but sampling can continue.

TABLE II. Summary of Detection Limits Used For House Analyses During The Love Canal EDA Full Air Study

Phase 1 N = 129	Chlorobenzene (ppb)	Chlorotoluene (ppb)
Average Detection Limits	1.0	1.2
Standard Deviation	0.5	0.5
Minimum Detection Limit	0.5	0.6
Maximum Detection Limit	3.7	4.2

Phase 2 N = 133	Chlorobenzene (ppb)	Chlorotoluene (ppb)
Average Detection Limits	0.7	0.8
Standard Deviation	0.2	0.3
Minimum Detection Limit	0.4	0.4
Maximum Detection Limit	1.6	2.3

Phase 3 N = 148	Chlorobenzene (ppb)	Chlorotoluene (ppb)
Average Detection Limits	0.9	1.2
Standard Deviation	0.2	0.4
Minimum Detection Limit	0.5	0.6
Maximum Detection Limit	1.8	2.7

Phase 4 N = 155	Chlorobenzene (ppb)	Chlorotoluene (ppb)
Average Detection Limits	0.7	0.9
Standard Deviation	0.2	0.3
Minimum Detection Limit	0.4	0.4
Maximum Detection Limit	1.5	2.1

Summary N = 565	Chlorobenzene (ppb)	Chlorotoluene (ppb)
Average Detection Limits	0.8	1.0
Standard Deviation	0.3	0.4
Minimum Detection Limit	0.4	0.4
Maximum Detection Limit	1.5	2.1

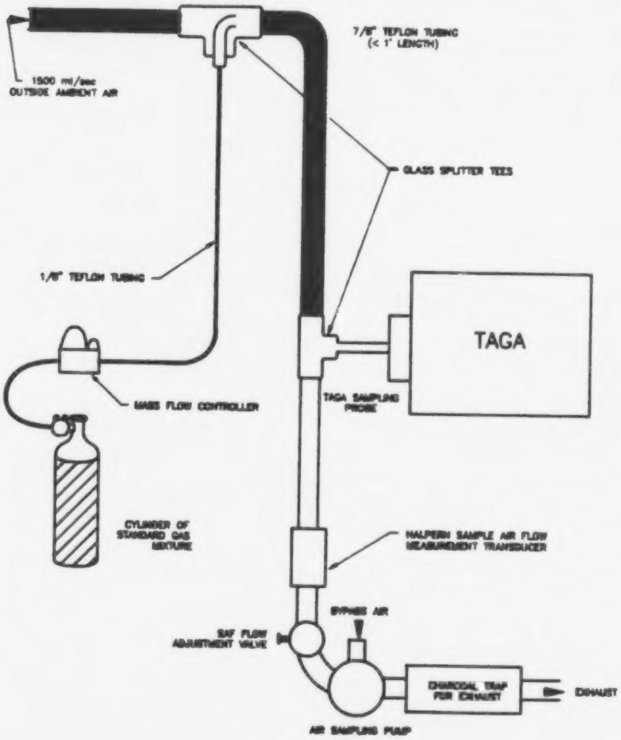
7/8" TEFLON TUBING
(< 1' LENGTH)
1500 ml/sec
OUTSIDE AMBIENT AIR
GLASS SPLITTER TEES
1/8" TEFLON TUBING
TAGA
MASS FLOW CONTROLLER
TAGA SAMPLING PROBE
CYLINDER OF STANDARD GAS MIXTURE
HALPERN SAMPLE AIR FLOW MEASUREMENT TRANSDUCER
BYPASS AIR
SAF FLOW ADJUSTMENT VALVE
CHARCOAL TRAP FOR EXHAUST
EXHAUST
AIR SAMPLING PUMP

FIGURE 1. Equipment Set-up for Performing TAGA Calibrations Using Standard Gas Cylinders.

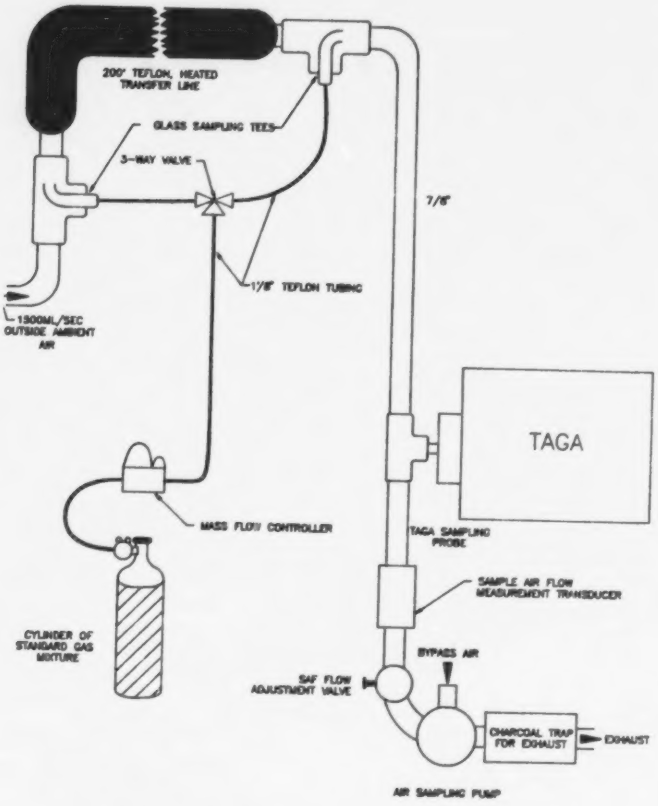
200' TEFLON, HEATED TRANSFER LINE
GLASS SAMPLING TEES
3-WAY VALVE
7/8"
1/8" TEFLON TUBING
1300ML/SEC OUTSIDE AMBIENT AIR
TAGA
MASS FLOW CONTROLLER
TAGA SAMPLING PROBE
SAMPLE AIR FLOW MEASUREMENT TRANSDUCER
CYLINDER OF STANDARD GAS MIXTURE
BYPASS AIR
SAF FLOW ADJUSTMENT VALVE
CHARCOAL TRAP FOR EXHAUST
EXHAUST
AIR SAMPLING PUMP

FIGURE 2. Equipment Set-up for Checking the Transport Efficiency of the TAGA Sampling Lines.

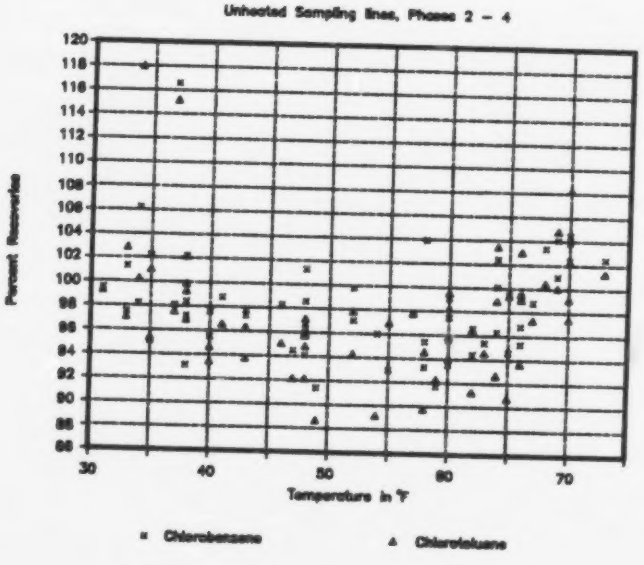

Figure 3. % Transport Eff. vs. Temp.

THE KWIK-SKRENE ANALYTICAL TESTING SYSTEM
Description of a tool for remediation of PCB spills.

G.R.Woollerton,S.Valin,J.P.Gibeault
Syprotec Inc.,Pointe Claire,Quebec.

INSTRUCTION

Soils and oils contaminated with PCB (polychlorinated biphenyl) threaten our environmental and economic well being. Public and private sectors of most North American communities strive to control PCB disposal and minimize the risks they pose to public health and property. Remedial reclamation of property is an important link in the chain of control. These efforts require tools. One of these is the KWIK-SKRENE ANALYTICAL TESTING SYSTEM, utilized to detect PCB contaminated soils and direct "clean up" efforts. KWIK-SKRENE gives the user an opportunity to economise on time and money. This paper presents the procedures, contents, and utility of the system.

The KWIK-SKRENE directs technicians to locate PCB contaminated soils and reduces the time and expense for laboratory analysis. It is not uncommon that conventional laboratory analyses and reports require more than one week to complete. Results from the KWIK-SKRENE may require only one hour, and as many as 40 test results can be obtained in an eight hour period.

The KWIK-SKRENE is a qualitative test that evaluates a soil extract for 10 ppm of Aroclor 1260 (a PCB) and provides information about the severity of the contamination. The test fits into essential analytical procedures of remedial action teams and has applications for oil, incinerator ash, and solid surface contaminations.

THE PROCEDURES AND CONTENTS OF THE KWIK-SKRENE.

The procedures for evaluating soils with the KWIK-SKRENE separate into two parts. After collecting samples, the technician must 1) extract the PCB and oil from the samples, then 2) analyze the extracts for PCB.

1) SOIL EXTRACTION

Sampling procedures will vary depending upon the protocols aadopted by different contractors, but it is assumed that the soil sample is in the form of a cylinder weighing 200 to 500 grams taken from the ground with a conventional core sampler. It is usually wet and contains stones and other debris. To properly test the soil, it must be dry and in a powdered state. This is achieved by cutting the sample down the long axis and, using one side, the sample is broken up, and stones, twigs, insects, and other debris removed. The sample is then put into a dish, dispersed and oven dried. A microwave oven dries a sample in two 2 minute cycles at 500 watts. Samples dried in convection ovens will require two hours at 105°C. The dried soil is then crushed with a mortar and pestle. 20 grams of soil is then mixed with 20 grams of extraction fluid and shaken on a mechanical shaker for 30 minutes. The extraction fluid is passed through a filter column and filter disc to remove chemical interferences aand particles. The filtrate that passes through is a clear oil ready for analysis.

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2) EXTRACT ANALYSIS

Analysis of the extract is performed with the standard KWIK-SKRENE colorimetric test for PCB in dielectric oils. 500 ul of Halogen reagent are added to 3 ml of extract, following by 1.5 ml of indicator buffer. Simmultaneously, the technician tests a "control" (supplied with the KWIK-SKRENE) that simulates a 10 ppm concentration. The control test is observed for a color change from yellow to mauve at which time the sample extract is observed. If the sample test remains yellow the extract contains less than the equivalent of 10 ppm Aroclor 1260. If it is brown, mauve, purple, blue or clear, it contains more than 10 ppm Aroclor 1260. The ultimate color of the sample test and the speed of color change depends upon PCB concentration.

CONTENTS OF A SOIL SYSTEM

The KWIK-SKRENE ATS for soils is supplied as a package containing all of the necessary hardware to extract and analyze soil samples including a mechanical shaker that is used for both test tubes or extraction bottles. 10 soil extractions and analyses can be performed simulataneously.

Other items included in the package are:

REUSABLE	DISPOSABLE
pipettors,	halogen regent
safety goggles,	Indicator buffer,
test tube racks,	test tubes,
timer,	control oil,
mortar and pestle,	pipet tips,
vacuum manifold and	pump gloves,
weighing scale	plastic bags,
case.	

CHEMISTRY OF THE KWIK-SKRENE

The physical chemistry:

PCB and oil are extracted from the soil using an aliphatic fluid(proprietary). PCB is very soluble in this fluid; more than 95% of the PCB is recovered from a fresh spill in 5 minutes. It does not dissolve inorganic salts or water than may interfere with the indicator chemistry of the test, but this insoluble matter may be carried in the fluid as a fine suspension or colloid. The fluid will dissolve organic acids and bases that may interfere with the indicator chemistry. To elimate most of these interferences the fluid is passed through an absorption column(proprietary) and a 0.45um pore size filter disc. The absorption column collects soluble interferences and the filter disc blocks suspended matter.

Wet Chemistry:

The KWIK-SKRENE indicator chemistry has two basic steps, 1.) The halogen reagent combines with PCB releasing chlorine and sodium atoms. 2.) The aqueous indicator buffer extracts the sodium chloride; then an oxidizing powder converts the chloride anions to chlorine which reacts with the yellow indicator turning it blue. The rate at which the color changes depends upon the concentration of PCB. For example, the 10 ppm control test changes color after five minutes whereas the change occurs in less time with more concentrated samples. It is possible for the experienced technician to qualify the concentration of a sample according to this rate of color change.

A NEW METHOD FOR THE DETECTION AND MEASUREMENT OF AROMATIC COMPOUNDS IN WATER

JOHN D. HANBY
HANBY ANALYTICAL LABORATORIES, INC.
HOUSTON, TEXAS

ABSTRACT

A Field Test Kit procedure for the rapid analysis of petroleum aromatic hydrocarbons over a wide range of concentrations in water and soil has proven of extreme utility in accurate assessments at spill sites, hazardous waste areas and underground storage tank removal locations. The kit was used to evaluate diesel oil concentrations at the Ashland Oil spill on the Monongahela and in conjunction with EPA studies of the oil concentrations in the Ohio river at Wheeling, West Virginia. A study of gasoline-in-soil at concentrations ranging from 5 mg/Kg to 10,000 mg/Kg was conducted. The colormetric results from the procedure in both water and soil are determined by comparison to a color chart.

UV/VIS spectrophotometric studies were performed to determine the relationship of concentration to color intensity (reflectance).

INTRODUCTION

In the introduction to his encyclopedic treatise Friedel-Crafts Alkylation Chemistry - A century of Discovery, Royston M. Roberts makes the statement, "probably no other reaction has been of more practical value." Professor Roberts goes on to say, "Major processes for the production of high octane gasoline, synthetic rubber, plastics and synthetic detergents are applications of Friedel-Crafts chemistry" (1984). It is fitting that, over a century after this monumental discovery, a technique for the analysis of environmental contamination caused by products of this reaction has been developed which employs the same chemistry.

The analysis of organic compunds in aqueous solution has long been recognized as problematical for many reasons. Primary among them of course is the fact of the limited solubility of such non-polar compounds in such an extremely polar solvent. In a recent laboratory study undertaken for the American Petroleum Institute on the solubilities of petroleum hydrocarbons in groundwater, it was pointed out that it was not possible to obtain linear response when trying to directly inject water standards of various aromatic hydrocarbons into a gas chromatograph (American Petroleum Institute 1985). This irreproducibility in analysis of water samples has been a source of consternation to proponents of gas chromatography for a long time. A fairly comprehensive review of the sort of problems associated with the gas chromatography of water samples is presented by Grob in Chapter 5 of Identification and Analysis of Organic Pollutants in water in their argument for the use of capillary versus packed column GC. A statement from that reference is particularly appropriate, "Environmental chemistry includes probably the most extreme branch of analytical chemistry.....environmental samples should be analyzed with means and methods to provide maximum separation efficiency and resolutions" (Keith 1981).

Certainly chromatography of all types has proven to be a technique of "maximum separation efficiency and resolution". With the advent of capillary columns of thousands of theoretical plates of separation efficiency the ability to resolve picogram quantities of substances is available. However, the problem of obtaining representative samples and their subsequent quantitative as well as qualitative analysis remains as perhaps the dominant problem in environmental assessment. Among the criteria involved in sampler design discussed by Johnson, et al, in a recent article in "Groundwater" are those which would "prevent changes in the analyte concentration due to: (1) sorption of degradation in the well; (2) changes in temperature or pressure; (3) cross-contamination between monitoring wells due to the sampling equipment"(1987).

Each of these criteria might also be applied not only to the collection of samples but to their analyses as well. In the subsequent laboratory analysis of a sample which may have been very well collected, preserved, and transported to the laboratory each of the above factors plays an analogous role: (1) sorption or degradation in the sampling container and analytical transference device, e.g., syringe, pipet, or beaker; (2) changes in temperature or pressure (particularly applicable to the extreme pressure/temperature changes occuring in the syringe and then the GC itself); (3) cross-contamination of syringes, purge and trap devices, sample lines, injectors, columns, and detectors.

The problem of sorption of organics in sampling devices and in the passage of samples through analytical tubing, was addressed in an article by

Barcelona, et al, in Analytical Chemistry. In that discussion, the sorption of various organic liquids in different organic materials is well documented (1985). This problem is seemingly one of a particularly Sisyphean nature, i.e., the containment of a substance within a like substance is akin to rolling a stone up a hill only to have it fall immediately down the other side. Certainly the problems encountered by the industry in attempting to contain petroleum products in unlined fiberglass tanks attests to this dilemma. The development of permeation tube calibration systems is based on the phenonmenon (O'Keefe 1966).

The present method addresses all of the problems mentioned in that, to put it most succinctly, it combines immediacy and simplicity of analysis. That is, it is easily transportable to the field which eliminates problems of sample transfer and storage, and it provides an immediate analysis of a large volume sample which speaks generally to the problem of representativeness.

THE EXTRACTION/COLORIMETRIC TECHNIQUE

The Hanby Field Test Method for aromatics in water described here comes in the form of a kit complete with necessary reagents and apparatus to perform immediate analyses at the groundwater well site. It is contained in a rugged plastic case with enough reagents to perform thirty field analyses. Within the case are contained: a 500 ml separatory funnel, a tripod ring stand, a 10 ml graduated cylinder, 2 reagent (liquid) bottles, one dessicant jar with 30 reagent (powder) vials, a color chart depicting test results for eleven typical aromatics, plastic safety glasses and 12 pairs of gloves. Upon arrival at the site the kit is opened and the tripod ring stand is assembled. A 500 ml water sample is introduced into the separatory funnel which is placed in the ring stand. Next, 5 ml of the extraction reagent is poured into the separatory funnel using the 10 ml graduated cylinder. The sample is vigorously extracted for two minutes with occasional release of the slight pressure build-up which occurs. The funnel is placed back in the ring stand and the extraction phase is allowed to separate to the bottom for five minutes. After phase separation is complete the lower extraction layer is drained into a test tube, allowing a small amount of the extraction solvent to remain in the separatory funnel. Then one of the reagent vials is opened and the contents immediately poured into the test tube. The tube is shaken for two minutes allowing the catalyst to be dispersed well throughout the extraction reagent so that color development, which is concentrated in the powder, will be uniform. Hue and intensity of the color of the catalyst which has settled in the tube is now compared to the standard aromatics pictured in the color chart.

The wide range of intense colors produced in Friedel-Crafts reactions has been observed since the discovery of this reaction. A brief description of the chemistry of the reaction, as well as the color involved, is given by Shriner, et al, in their widely used book (1980). In this novel adaptation of Friedel-Crafts alkylation chemistry, one of the reactants, the alkyl halide is used as the extractant. The alkyl halide extractant plus the aromatic compound present in the water sample are caused to form electrophilic aromatic substitution products by the Lewis acid catalyst which is added in great enough amount to also act as the necessary dehydrant to allow the Friedel-Crafts reaction to proceed. These products are generally very large molecules, i.e., phenyl groups clustered around the alkyl moiety, which have a high degree of electron delocalization. These two factors are the principle reasons for the extreme sensitivity of this procedure. That is, large molecules are produced which are very intensely colored.

In the field conditions where this procedure is by and large carried out the reaction is exposed to sunlight. This means that there will be a window in which to observe the color that is produced. This is because of the general instability of the reaction products to photochemical oxidation. Strong sunlight will cause most of the colors produced to fade to various shades of brown within just a minute or two; therefore, it is advisable to perform the test in a shaded area.

APPLICATIONS OF THE METHOD

Obviously, this method will have a wide variety of applications in field investigations. In fact, utilization of the Hanby Field Test by an environmental testing company has been going on since August, 1987. Site investigations of hazardous waste-containing landfills and underground storage tank leaks have been conducted in several states thus far and use of the kit has greatly facilitated sampling site locations. The first field use of the kit was in the establishment of groundwater monitoring well locations at an organic chemical processing unit. An article describing this first field use of the method is inpreparation.

Recent regulations for the monitoring of underground storage tanks require that soil/groundwater investigations be carried out regularly to insure that no leakage has occured. It can be seen that the use of this technique shich is easily learned and can be performed at an extremely low cost will provide an immediate and defenitive answer to these requirements.

OHIO RIVER STUDY

In the evening of January 2nd, 1988, the collapse of a tank containing approximately 3.5 million gallons of diesel fuel precipitated one of the worst inland oil spills in the country's history. Approximately one million gallons of the oil washed in a huge wave over the containing dikes around the tanks at the Ashland Oil Plant at West Elizabeth, Pennsylvania and into the Monongahela River.

Monday morning, two days after the spill, I contacted Mike Burns of the Western Pennsylvania Water Company in regard to using the Hanby Field Test Kit at the company's water treatment facility on the Monongahela south of Pittsburgh. Mike asked me to bring one of the kits to the plant. The next day I flew into Pittsburgh and was met by Mike at the West Penn Water Works Treatment facility where I demonstrated the use of the kit for the personnel at the plant. Then Mike suggested I call John Potter, the chief chemist at the Water Treatment Plant in Wheeling, West Virginia which was the next major facility taking water from the Ohio river. John said the kit sounded like it would fill a real need for a rapid analysis of the river water at the plant's intakes. The next day, Wednesday, I was demonstrating use of the kit to the personnel at Wheeling. It was immediately put into use on an around-the-clock basis when they realized that in just a few minutes they could get visual indication down to 100 ppb of the diesel aromatic components.

The next morning I met with the West Virginia Department of Natural Resources personnel who were in Wheeling to monitor the oil spill. That afternoon I was invited by the office of the EPA in Wheeling to join EPA chemist Bob Donaghy, West Virginia Department of Natural Resources Inspectors Sam Ferris and Brad Swiger, and the Ohio River Valley Water Sanitation Commission Coordinator of Field Operations Jerry Schulte on the river tugboat Debbie Sue to make a run up the Ohio River from Wheeling to try to locate the front of the spill.

The investigators met at the Debbie Sue at noon where it was tied up at the docks on the south side of Wheeling. A light snowfall had begun and the temperature was around 10°F as the boat pulled out into the Ohio, headed up stream.

Due to the fluctuating voltage from the tug's generator the fluorometer readings exhibited a fairly wide swing during the ensuing measurements. As for the measurements performed with the Field Test Kit, I was primarily concerned with the sensitivity of the test in relationship to the near-zero temperature of the water. Reference to the API study of solubilities of petroleum hydrocarbon components in groundwater had indicated rather large decreases in partitioning of these components into water at lower temperatures.

There was no time, however, to spend worrying about these matters of close quantitation. The boat was soon into the channel and Jerry Schulte was bringing aboard the first bailer of water. On the first sample taken, just minutes after leaving the dock, an obviously detectable coloration was seen in the catalyst material of the Field Test. Reference to the color chart indicated presence of aromatic constituents at something less than 0.5 ppm diesel. Having no reference colors or data at these temperatures I arbitrarily chose this intensity to represent 0.1 ppm. The fluorometer was bouncing between zero and four on its moveable dial indicator. (It was an old Turner model arbitrarily numbered from 0 to 100.)

We continued approximately eighteen miles up the Ohio taking samples from the surface and the bottom on the West Virginia side, mid-channel, and the Ohio side. As table 1 indicates the results from the EPA fluorometer and the Hanby Field Test Kit tracked each other fairly consistently at each point.

TABLE 1

Ohio River Sampling For Diesel Oil
January 7, 1988

Ohio River Mile Point	Fluorometer Reading	Hanby Field Test (ppm)
89.0	4	0.10
85.5	8	0.15
85.5	9	0.15
85.5	6	0.20
85.0	8	0.20
85.0	11	0.20
84.5	6	0.20
84.5	10-15	0.50
84.5	10	0.20
82.0	20	1.00
81.0	25	1.00
80.0	30	1.50
79.0	33	2.50
77.0	57	10.00
76.0	43	8.00
75.0	35	7.00
74.0	48	5.00
70.0	29	3.00

SOIL STUDIES

Site investigations at leaking underground storage tanks, hazardous waste sites, surface spills, etc. normally involve at least prelimary evaluations of the soil prior to the installation of monitoring wells. The use of the Hanby Field Test Kit for soils has found wide application in this regard which has proven to be far superior to methods such as soil gas techniques involving the use of OVA's or field portable chromatographs to sniff the headspace of samples.

The technique developed at Hanby Analytical Laboratories for use of the kit is as follows:

1. Place 200 grams well-crumbled soil in a quart jar.
2. Add 500 mil of distilled water and shake well for 15-20 minutes so that water/soil is very well mixed.
3. Pour mixture into a 1 liter Imhoff cone. Sprinkle 2 level tablespoons powdered ferrous sulfate into soil water mixture. Allow mixture to clarify for thirty minutes.*
4. Decant clarified portion into the Field Test Kit separatory funnel and perform the FTK extraction/colorimetric test.

* Place a piece of Parafilm or aluminum foil over each Imhoff cone to keep volatilization losses minimized.

A study of two different soil types was undertaken using super unleaded gasoline at various concentrations. The studies illustrated in the slides are:

1) a typical Texas "Gumbo" topsoil containing: 0 (Blank), 10, 50, and 200 mg gasoline mg/Kg 2) a deeper sandy soil containing: 0, 5, 25, 100, 500, 2500, and 10,000 mg/Kg.

Soil samples were first sifted and homogenized to remove twigs, leaves, rocks, etc. 200 gram portions of each soil type (4 for the top soil and 7 for the sandy soil) were weighed into quart mason jars. Appropriate amounts of gasoline were injected directly onto the soil using microliter syringes with the solvent flush technique. The soil/water mixture was shaken in the capped jars over a ten minute period. 500 ml of de-ionized water was added to the jars which were then shaken periodically over a thirty minute period. The soil/water mixture was poured into the Imhoff cones and 5 ml. finely ground ferrous sulfate heptahydrate was shaken into each. The ferrous sulfate was very effective in settling the suspended matter and clarification of approximately 300 ml of the supernatant water was achieved in thirty minutes. 250 ml. of the supernatant was employed in the subsequent Hanby Field Test Method.

UV/VIS SPECTROPHOTOMETER STUDIES

Determinations of principle wavelengths and reflectance data were made in correspondence with aromatic compounds depicted on the color chart. These investigations were conducted by preparing a range of concentrations of selected aromatic compounds, performing the Hanby extraction/colorimetric procedure and then immediately measuring the reflectance of the catalyst.

METHOD

Ten parts-per-million (vol/vol) solutions of benzene, toluene, o-xylene, special unleaded gasoline, naphthalene and diesel were prepared by injecting 20 microliter amounts of each compound into 2.0 liters of de-ionized water at 20°-21°C and stirring for one hour. Dilutions from the stock solutions were prepared to 0.01, 0.02, 1.0 and 5.0 ppm. The extraction/colorimetric procedure employed with the Field Test Kit was modified to fit the requirements of the UV/VIS reflectance apparatus. Four ml of the extraction reagent were used to extract the water samples for two minutes. The extraction solvent was then drained into a cuvette. Two grams of the catalyst material was added to the cuvette which was covered with its teflon cap, and the mixture was shaken vigorously for three minutes. The cuvette was placed in the spectrophotometer and scanned over a range of 350 nm to 600 nm.

INSTRUMENTAL PARAMETERS

For this study a Varian DMS 300 UV/VIS spectrophotometer was utilized. Instrument settings were: Slit width 2 nm, tungsten source, scan rate 50 nm/min. All of the scans were corrected to 100% transmittance baseline using a blank sample which was scanned in reference to a barium sulphate reflectance disk. The sample compartment was fitted with a diffuse reflectance accessory which was modified by blocking out the top portion of the light path so that only the catalyst in the bottom half of the cuvette would be scanned.

DISCUSSION

Figure 1 shows the spectrograms for each of the six substances scanned. The concentration for each of the plots is as follows (ppm by volume): A=0.1, B=0.2, C=1.0, D=5.0, E=10.0. These concentrations exhibit well defined differences in the traces of their reflectance curves for each of the substances.

Figure 2 shows the reflectance trace for differerence concentrations of benzene. These concentrations are (ppm by volume): A=0.01, B=0.05, C=0.25, D=1.0. These runs were scanned on the spectrophotometer from 250 nm to 700 nm at different instrument settings: slit width = 1.0 nm, scan rate = 20 nm/min., smoothing constant = 5 (sec). The different instrument parameters plus the fact that a special cuvette was constructed to cover a larger area of the reflectance opening contributed to the greatly enhanced differences in the traces at these, even lower, concentrations.

CONCLUSIONS

The development of a field method for the analysis of organic contaminants at sub-part-per-million levels in water has been proven to be a valuable tool in the establishment and the sampling of groundwater monitoring wells. The accuracy of the method has been proven to far exceed that of direct injection gas chromatography. A rapid soil-wash method has also been developed employing the Hanby Field Test Kit technique which has proven to be effective on top and deep soils over a range of 5 mg/Kg to 10,000 mg/Kg gasoline in soil. Development of instrumental spectrophotometric techniques will allow even greater sensitivity and qualitative analysis of aromatic contaminats in soil and groundwater.

A variation of the procedure involving the extraction of a sample with an aromatic solvent and then addition of the Lewis acid catalyst allows for the determination of the presence of alkyl halides, e.g. trichloroethylene. In this version of the test a reflectance adaptor for the spectrophotometer is not necessary since the color is not concentrated in the catalyst but is developed in the extractant solvent.

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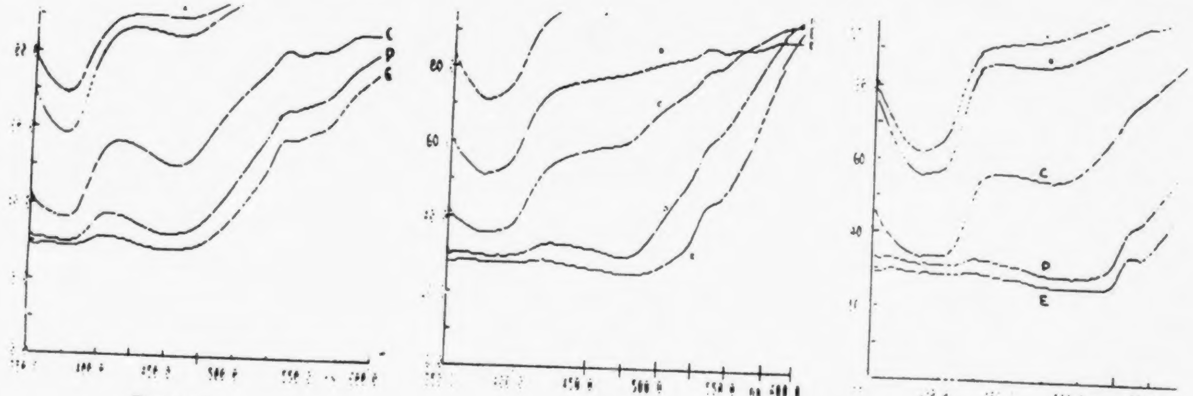
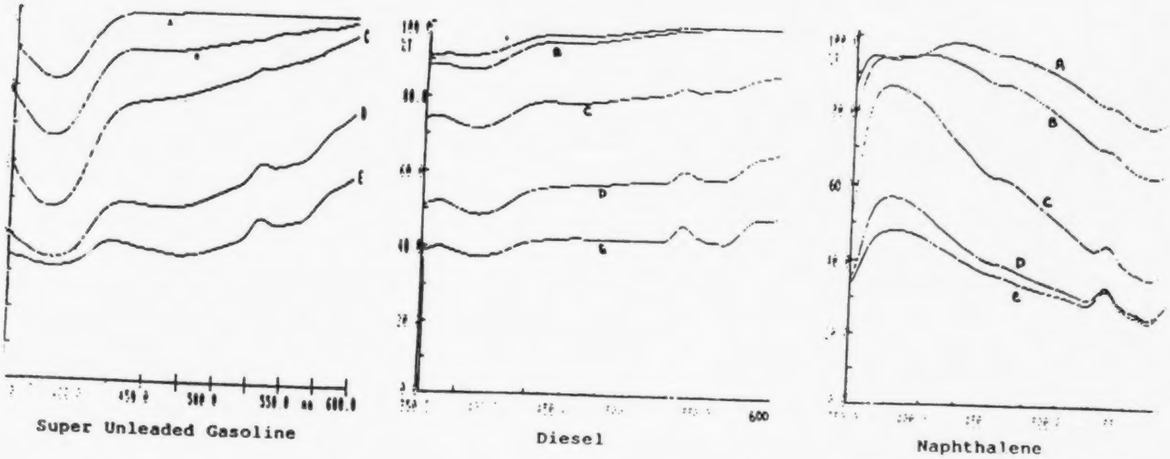


Benzene

Toluene

o-Xylene



Super Unleaded Gasoline

Diesel

Naphthalene

Figure 1

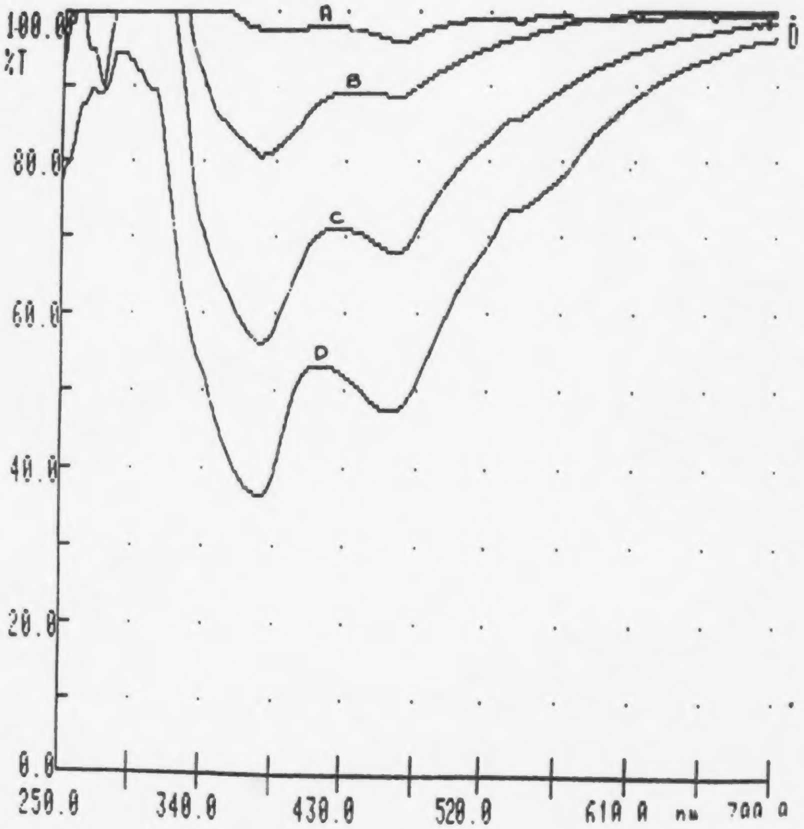

100.0
%T
80.0
60.0
40.0
20.0
0.0
250.0
340.0
430.0
520.0
610.0
nm
700.0
A
B
C
D
D

Figure 2

DEVELOPMENT OF A TEMPERATURE PROGRAMMED MICROCHIP, HIGH RESOLUTION GAS CHROMATOGRAPH/MASS SPECTROMETER FOR VOLATILE ORGANIC COMPOUND ANALYSIS

E. B. Overton, E. S. Collard, H. P. Dharmasena, P. Klinkhachorn and C. F. Steele
Institute for Environmental Studies
Louisiana State University
Baton Rouge, Louisiana 70803

ABSTRACT

The interfacing of a temperature programmed microchip gas chromatograph with a mass spectrometer has developed to produce a field deployable analytical system capable of rapid, laboratory type analyses of ambient air samples for volatile organic compounds. The addition of a microprocessor based temperature controller for temperature control and temperature programming of the analytical column (utilizing a small thermoelectric heat pump) has enhanced the performance of this system for quantitative analysis. Programming the solid-state microchip gas chromatograph column oven below ambient temperature at the beginning of the analytical run and then upwards to a higher than ambient temperature during the analytical run yields acceptable wide peak widths at the beginning of the analytical run and sharper peaks during the course of the analysis when compared to isothermal analyses. The temperature programming and control of the gas chromatographic liquid phase improves the sensitivity and peak shapes of all of the compounds during an analytical run.

INTRODUCTION

A microchip gas chromatograph produced by using silicon micromachining technology has been discussed in another paper (1). The development of these small devices has produced analytical instruments which can perform complex separations of volatile mixtures with analysis times of two to three minutes. On-site environmental operations, whether hazardous waste-site clean-up or hazardous materials spill mitigation, require extracting the most information from a sample in the least amount of time. The need to produce laboratory quality analyses with short sample turn around times prompted us to consider the interfacing of a microchip gas chromatograph with a mass spectrometer to produce an analytical system for the analysis of volatile organic compounds.
Temperature programming of the analytical column, a technique which has long been recognized as a method of improving analytical performance, was used as a means of reducing run time and optimizing chromatographic peak widths. Programming of the solid-state microchip gas chromatograph column oven below ambient temperature at the beginning of the analytical run then upwards to a higher than ambient temperature during the analytical run produces acceptable wide peak widths at the beginning of the analytical run and sharper peaks during the course of the of the analysis when compared to isothermal analyses.

MATERIALS AND METHODS

A modified microchip gas chromatograph (Michromonitor 500, Micro Sensor Technology, Inc., Freemont, California) was interfaced with an ion trap mass spectrometer (Finnigan Model 700 Ion Trap Detector, Finnigan MAT, San Jose, California) to function as a small, rapid gas chromatograph/mass spectrometer (GC/MS) system. The combination of these two instruments allows for rapid mass spectral identification and quantification using extracted ion current profiles of volatile organics in environmental samples.

The mass spectral operating parameters, including the tuning procedure, were as outlined in the operating manual for the Ion Trap Detector. The scanning rate of the mass spectrometer was set at the maximum rate of 4 scans per second from 45 to 246 AMU. The lower limit of 45 AMU was chosen to eliminate the problem of scanning over components in the air peak. The upper limit of 246 AMU was used to allow adequate spectra acquisition for most (10 volatile priority pollutants and similar compounds) of the compounds which the microchip gas chromatograph is capable of analyzing. The microchip gas chromatograph was adjusted to provide a flow of approximately 4 ml per minute through the analytical column. The analytical column (1 meter X 0.23 mm i.d. DB-1) was wound into an aluminum column jig which was mounted onto the chromatographic module with a specially developed zero-dead volume fitting. The free effluent end of the column (which normally goes to the detector of the microchip gas chromatograph) was attached to the open split interface of the mass spectrometer.

A Peltier' device (thermoelectric heat pump) (2) was chosen to supply the heating and cooling required for temperature programming of the column. A microprocessor based (Intel 8751 single chip microprocessor) controller was designed and built in our laboratory to provide electronic control of the

Peltier' device. The temperature programmer (Peltier' device and controller) uses only electrical current and does not require liquid cryogenic coolants to control the column temperature below ambient temperature. The Peltier' device along wilth its heat sink was mounted on one side of the column jig (Figure 1). A temperature sensor (Analog Devices AD-590) was mounted on the other side of the column jig to measure the temperature of the column assembly and provide information for the temperature controller. The Peltier' device along with the controller is capable of set point temperature control (± 0.05°C) from -5°C to 90°C or temperature programming (±0.6°C) of the analytical column from 2°C to 80°C. Temperature ramping speeds range from 0.1°C to 1°C per second with good reproducibility, however, 0.8°C per second is as fast as practical for true linear programming (Figure 2).

RESULTS AND DISCUSSION

The isothermal gas chromatograph mass spectrometer with the microchip gas chromatograph functioned well while operating at ambient temperature (approximately 25°C), however, the early eluting peaks were so narrow (3-4 mass scans across the peak) that precision of the quantitative data was not acceptable even though the mass spectrometer was scanning as rapidly as possible (4 scans per second from 45 to 246 AMU) over the mass range selected for the analysis (Figure 3). It was belived that if the chromatography was controlled such that the early eluting compounds would exhibit peak widths on the order of 7-8 scans (approximately 2 seconds) the quantitative information for these compounds would then become more precise. Complete chromatographic separation of each component in the mixture was not considered as important as improved quantitative ability since standard mass spectral data manipulation techniques can be used to identify components and quantitation can be obtained from extracted ion current profiles.

Qualitative identification of the compounds run on the system was good in that the mass spectrometer was able to distinguish between two compounds eluting in the same chromatographic peak. Several combinations of temperatures and ramping speeds as well as delay times (starting the temperature ramp at some time after the injection is made) were investigated. The best results were obtained by starting the analytical column temperature at 2°C and ramping the temperature at 0.8°C per second to 80°C starting immediately at the time of injection. Comparing the chromatographic runs with and without temperature clearly shows increased peak widths for early eluting peaks (Figure 4). This increased amount of time in which the mass spectrometer is allowed to obtain data from a given chromatographic peak provides more accurate integration of the peak area. More accurate quantitative information from the analysis is possible.

CONCLUSIONS

The interfacing of the microchip gas chromatograph and the ion trap mass spectrometer has proved to be an excellent system for the rapid analysis of volatile organic compounds in environmental samples. The sensitivity of the system is approximately 0.5ppm (volume/volume in air) for most of the volatile compounds studied. Pre-analysis concentration techniques such as trapping on adsorbents with thermal desorption can increase the detection limits to 1ppb. Temperature programming of the analytical column of the gas chromatograph increases the precision of the quantitative information for all compounds. Rapid sample turn around time as well as laborabory type analytical results are possible with this system. Special sample treatment is not necessary and there are no adsorbants or solvents used with this system. Actual use of the system in an air monitoring program has demonstrated excellent results that allows sample turn around times of approximately five minutes.

ACKNOWLEDGMENTS

The financial support for this work from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce, Contract No. 50-ABNC-7-00100, is gratefully acknowledged.

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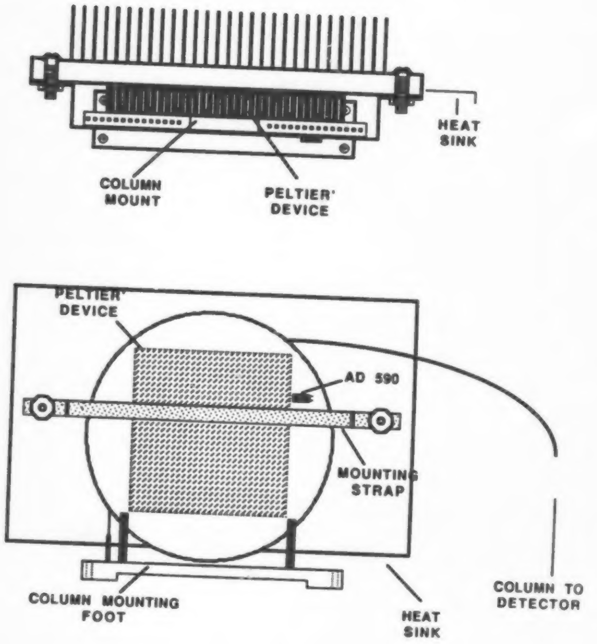
HEAT SINK
COLUMN MOUNT
PELTIER' DEVICE
PELTIER' DEVICE
AD 590
MOUNTING STRAP
COLUMN TO DETECTOR
COLUMN MOUNTING FOOT
HEAT SINK

Figure 1. Construction of Microchip GC Column Oven

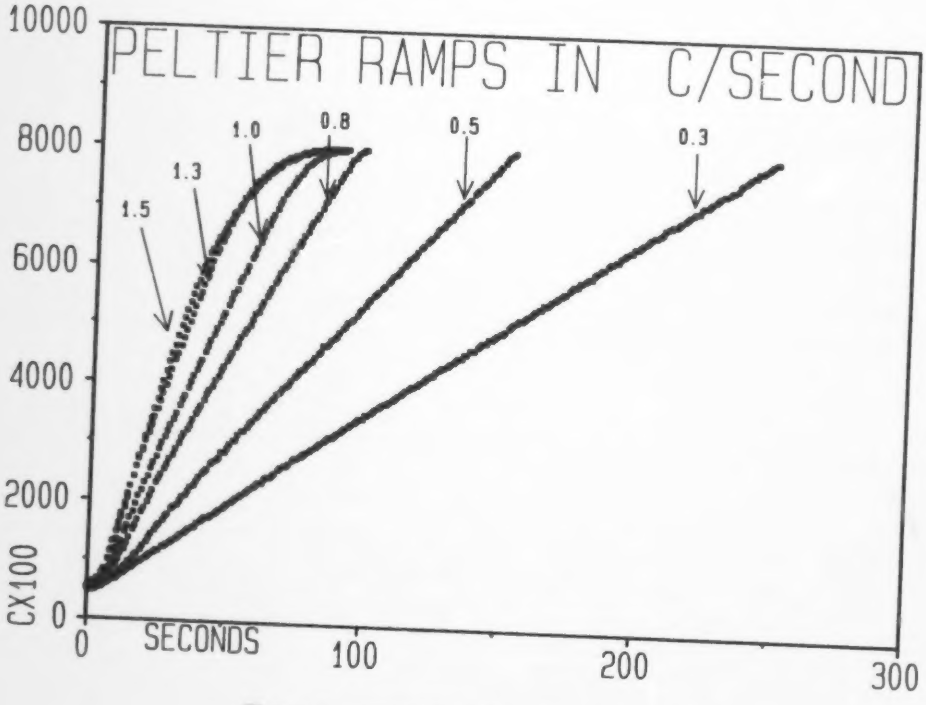

Figure 2. Temperature Ramps of Peltier' Device

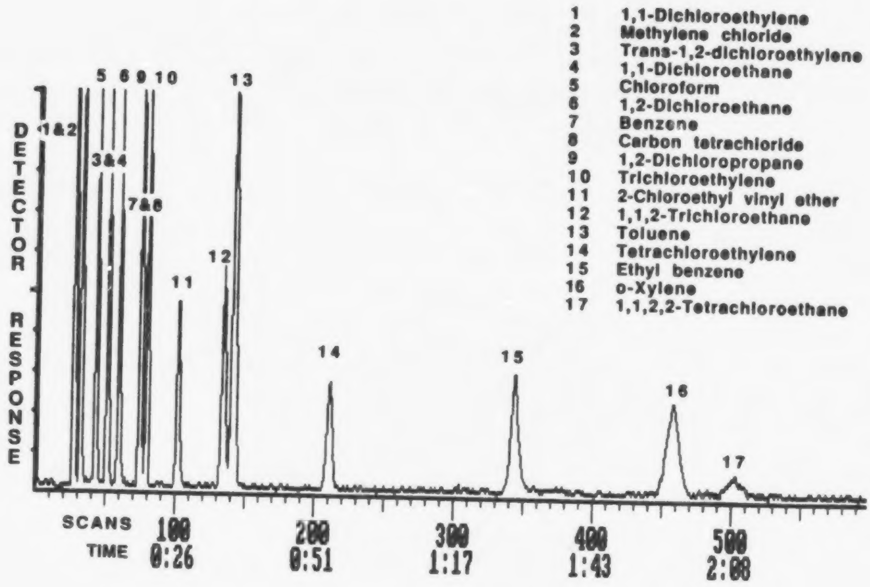

Figure 3. 17 Component Volatile Organic Mixture from Microchip GC/MS

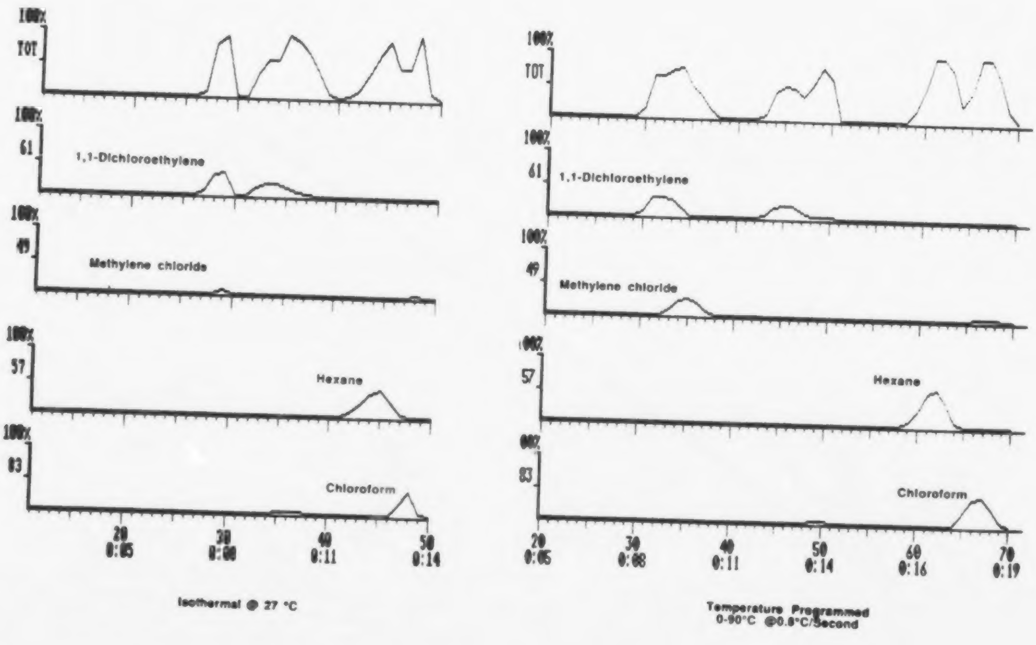

Figure 4. Comparison of Peak Widths

APPLICATIONS OF THE PYRAN THERMAL EXTRACTOR-GC/MS FOR THE RAPID CHARACTERIZATION AND MONITORING OF HAZARDOUS WASTE SITES

C.B. Henry and E.B. Overton
#42 Atkinson Hall
Institute for Environmental Studies
Louisiana State University
Baton Rouge, LA 70803

C. Sutton
Ruska Instruments
P.O. Box 742688, Houston, TX 77274

The Pyran Thermal Extractor-GC/MS instrument is, in essence, a robotic device that both extracts and analyzes semivolatile analytes in solid matrix samples. It is capable of many analytical applications that currently require CLP-type analytical techniques. The instrument is designed to be rugged enough for field deployment. In this paper, we provide data to demonstrate the applicability of thermal extraction techniques using the Pyran system on soils/sediments and semi-solid sludges. The instrument is a qualitative and quantitative tool for rapid chemical analysis of a variety of sample types. The detection limit for the PAH phenanthrene in soil/sediment samples is estimated at 10 ppb (ng/g).

INTRODUCTION

Site investigations and cleanup activities under Superfund often require the rapid analysis of samples for semivolatile hazardous substances in order to make on-site decisions. Historically most Superfund analytical data has been generated through the Contract Labortory Program (CLP) whose methods involve the complex extraction, cleanup, and analysis and are outlined in EPA's CLP protocols under Superfund and SW-846 analytical protocols under RCRA. These methods are time consuming and expensive. The instrument investigated here has an analytical turn- around time for base-neutral and acid-extractable compounds of slightly longer than one hour, and no sample preparation other than weighing the sample is required.

In this paper, we experimentally investigate the possible use of thermal extraction-GC/MS techniques for the rapid extraction and analysis of semivolatile organic compounds in soil and sediment samples. The instruments used were the Pyran Level I Thermal Extractor/Flame Ionization Detector (FID) and the Level II Thermal Extractor/Mass Spectrometer. Each has a chemically inert all quartz thermal extractor. The Level I extractor is interfaced directly to a FID, while the Level II is interfaced to an all quartz cold trap and a fused silica capillary GC column which elutes into an ion trap detector. The instruments were developed to meet the rugged analytical needs of petroleum exploration. We feel this makes them ideally suited for field applications with only slight modifications[1].

The Level I unit produces a thermal extraction profile, plot of temperature vs detector response, and is a useful tool for rapid screening of samples. The Level II provides quantitative and qualitative information about samples which we will demonstrate is generally comparable to data from conventional Contract Lab Program (CLP) type analyses.

A 25 component calibration standard was analyzed to demonstrate the sensitivity and quantitative linearity of the instrument; 22 of the 25 compounds are EPA Target Compounds. In addition, samples from various environmentally impacted sites were analyzed to demonstrate the applicability of the instrumentation in the rapid analysis of "real world" (as opposed to laboratory spiked) samples. Wet and dry sediment samples were analyzed to asses the affect of moisture content on the thermal extraction process. Pentachlorophenol contaminated creosote sludges from 2 sites (referred to in this paper as sludge A and sludge B) and a sediment sample contaminated with diesel oil were analyzed on both the Level I and Level II instruments. Thermal extraction analyses of the sediment sample were compared with samples analyzed by established analytical methods.

EXPERIMENTAL METHOD

Soil and sludge samples were prepared for analysis by weighing a small aliquot of the sample into a porous quartz "cup" and placing it into the pyrocell loader. No other sample preparation was required. A small amount of the sediment sample was air dried before analysis by placing the wet sediment in a scintillation vial which was then placed in a plain glass desiccator filled with $CaSO_4$ overnight. None of the sediment samples were treated in any manner to enhance the homogeneity of the sample. The calibration standards were in solution with methanol and were added to the lid of the quartz cup by a syringe technique. The 6-point standard curve ranged from 6.4 ng to 600 ng applied to the quartz cup.

The level II instrument was configured with a 15 meter DB-5 capillary column (0.25 mm ID and 0.25 micron film thickness from J&W Scientific Co.). The column was interfaced to a Finnigan MAT Ion Trap Detector (ITD) via an open split interface, and the ITD was operated in the scanning mode over a mass range of 47-507 amu using automatic gain control (AGC) software.

The Level I instrument was temperature programmed from 30°C to 500°C at a temperature rate of 30°C/min. Flow rates for the He carrier gas, H_2, and zero air were 60 mL/min, 55 mL/min, and 550 mL/min, respectively. Nelson 2600 chromatographic software was used for data processing of the FID response. Quantitative analyses was by an external standard method using response factors estimated from phenanthrene or n-C_{32}.

The Level II instrument was operated by the following technique: The pyrocell was set at an initial temperature of 30°C then increased to 240°C at 30°C/min to thermally extract the analytes then cooled to 30°C at 30°C/min. The capillary column was initially set to -35°C and held for 13 min to cold-trap the analytes then temperature programmed to 300°C at 5 C/min and held for 10 min. The ITD was turned on 21 min into the analysis. The trap and split were maintained at 330°C and 300°C, respectively. The split ratio was set for a 1:40 split. The total analysis time was 84 min. Quantitations were by an external standard method using authentic standards when available.

When wet sediment samples were analyzed in the Level II instrument, the pyrocell temperature program was slightly modified to hold the pyrocell at 60°C for 5 min with the vent open. This is required to prevent ice formed from closing off the capillary column.

The conventional GC/MS analyses were performed by an organic extraction method outlined by the National Oceanic and Atmospheric Administration (NOAA) for use in the National Status and Trends Program[2]. The nomenclature "conventional" refers to solvent extraction techniques in this paper. The extracts were analyzed on a Hewlett-Packard 5890 GC equipped with a 30 M J&W DB-5 column directly interfaced to a Hewlett Packard 5970B mass spectrometer. The report values were corrected for recovery using the surrogate standard hexamethylbenzene.

RESULTS AND DISCUSSION

Standards

The 25-component, 6-point standard curve was linear and demonstrated good sensitivity. Table 1 lists the compounds analyzed in the standard, the mean retention time in scan numbers for each component, the percent relative standard deviation (%RSD) of the retention time for 6 analyses, and the correlation coefficient (R) of the detector response vs amount of analyte (response factor). The range of R was 0.82-1.00, and the mean value was 0.96. Representative standard curves are shown in figure 1. Figure 2 shows the Total Ion Chromatogram (TIC) of a calibration standard analysis from scan 400 to scan 900. The instrument has a detection limit for phenanthrene of less than 1 ng. If this value is extrapolated for a 100 mg sediment sample, the detection limit for phenanthrene would be in the 10 ppb range.

Sludge Samples

From the thermal chromatograms produced by the Level I analyses and shown in Figure 3, it appeared that sludge B contained higher molecular weight contaminates than sludge A. The level II analyses of the same sludges supported the results from the Level I screening analyses (Figure 4). In both analyses, the compound specific determination of the semivolatile contaminants was rapidly assessed. Sludge A contained a typical unresolved complex mixture with resolved normal aliphatic hydrocarbons and a high concentration of pentachlorophenol. Octachlorodibenzo-p-dioxin and the two heptachlorodibenzo-p-dioxin isomers were also detected. Sludge B contained a much greater concentration of polynuclear aromatic hydrocarbons than A. These two preliminary analyses indicate that the Level II instrument is a useful tool in the rapid assessment of hazardous waste sludges typical of those associated with Superfund and Nonhazardous Oilfield Waste (NOW) sites.

Diesel contaminated sediment sample

The Level I analysis of the diesel contaminated sediment (sediment A) is shown in figure 5 compared to a control soil sample which contains only normal background organic constituents, which we believe are primarily pyrolysis products of high molecular weight organic compounds. The concentration of hydrocarbons in the diesel contaminated sediment was estimated at 5.8 µg/mg by an external standard quantitation method using a response factor calculated from n-C_{32}. The heavier molecular weight components, those extracted after 13 min of analysis time and typically associated with the natural organic content of the sediment, were not quantitated.

Figure 6 contrasts a conventional solvent extraction followed by GC/MS analysis to a Level II analysis of dry and a wet diesel contaminated sediment (48% moisture by weight). Each analyses contained an unresolved complex mixture (chromatographic hump) with resolved normal aliphatic hydrocarbons from n-C_{13} to n-C_{23}. The precision of the analyses using the Level II instrument was compared to that of conventional solvent extraction GC/MS analyses. Four duplicate Level II analyses of the sediment were compared to two duplicate conventional extractions and GC/MS analyses. Each extract was analyzed twice. The mean recovery of the conventional analyses was 77%. The quantitative results for selected components are given in table 2. The mean %RSD of the thermal extraction analyses was 20.60 compared to 19.51 for the conventional analyses. From this limited set of analyses, it appears that the precision of the thermal extraction technique using the Pyran system is comparable to that obtained through conventional solvent extraction GC/MS techniques. A significant but unknown portion of the deviation between sample analyses is the natural variability of environmental samples. The sediment was not treated in any manner to enhance its homogenity. It was intended to be representative of moderately contaminated environmental samples.

The mean value of phenanthrene determined using the Level II instrument was 3.1 ng/mg compared to 4.6 ng/mg as determined by a quadropole mass spectrometic analysis. From repeated analyses of the sample aliquot, we estimate that 95% of the phenanthrene was removed in the initial thermal extraction.

There seems to be no substantial loss of the lighter molecular weight components in the wet sediment when analyzed by the Level II instrument. In general, the calculated quantities were less than the mean determined from the dry sediment analyses by 27%. However this may in part be due to physical obstruction of the carrier flow when the sediment dries as a solid plug in the quartz cup encapsulating part of the sediment. The wet sample analysis was intended to represent a worst case scenario, as the sample cup was pack completely full with 180 mg wet sediment. The percent moisture was determined by standard methods to be 48%.

CONCLUSION

In conclusion, the Pyran Thermal Chromatograph (Level I) and Thermal Extractor-GC/MS (Level II) is capable of providing rapid semivolatile organic analysis of most solid and semi-solid samples that are encountered at Superfund sites. The robotic characteristics of the instrument reduce the analysis time associated with conventional solvent extraction methodologies. The instrument has a sample turn around time of approximately 1.5 hours with detection limits in the low parts per billion range. Further methods development and evaluation is required to fully asses the potential of this technique for both laboratory and field deployable analytical applications.

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(1) Overton, E.B. and S.J. Martin; "A field deployable analytical instrument for the analysis of semivolatile organic compounds of Superfund sites," Proceedings of the Third Annual US EPA Symposium on Solid Waste Testing and Quality Assurance. 1987. Vol. II, p. 8-55.

(2) MacLeod Jr., W.D., and et al. Standard Analytical Procedures of the NOAA National Analytical Facility, 1985-1986. NOAA Technical Memorandum NMFS F/NWC-92.

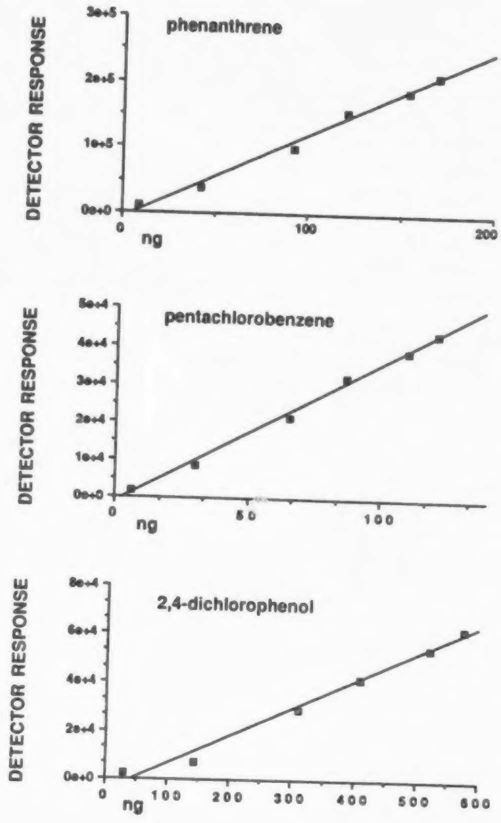

Figure 1 Representative standard curves.

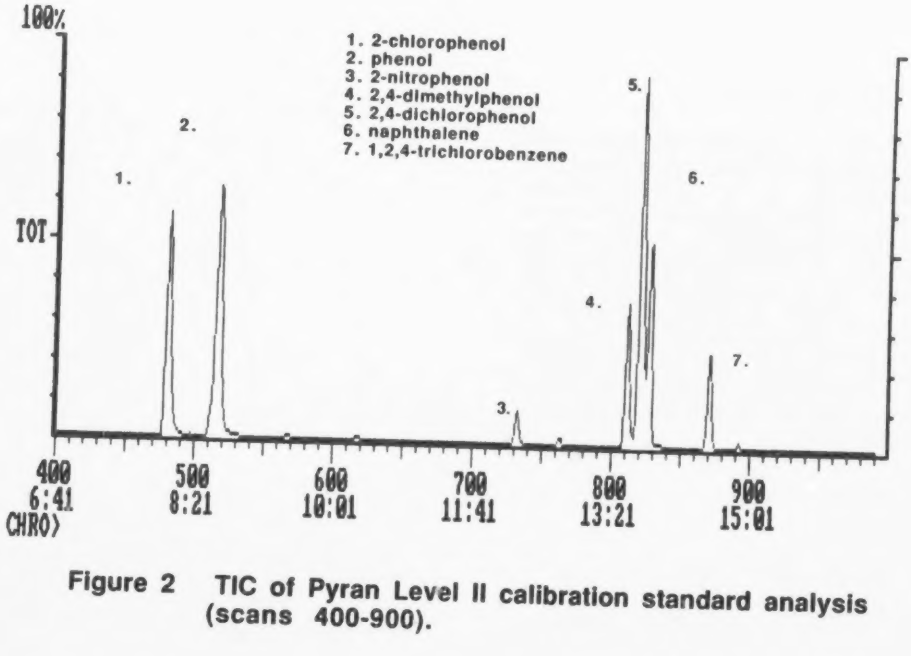

Figure 2 TIC of Pyran Level II calibration standard analysis (scans 400-900).

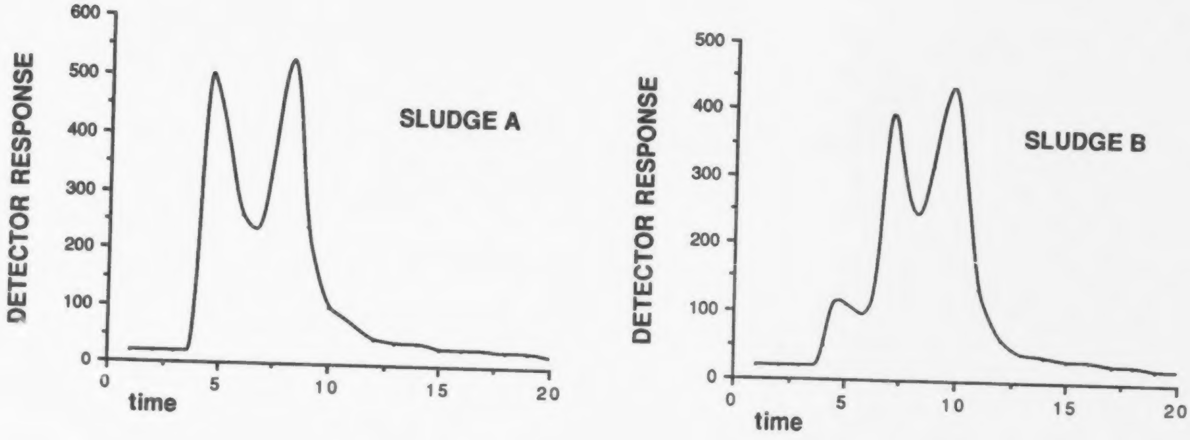

Figure 3 Level I thermal extraction profiles.

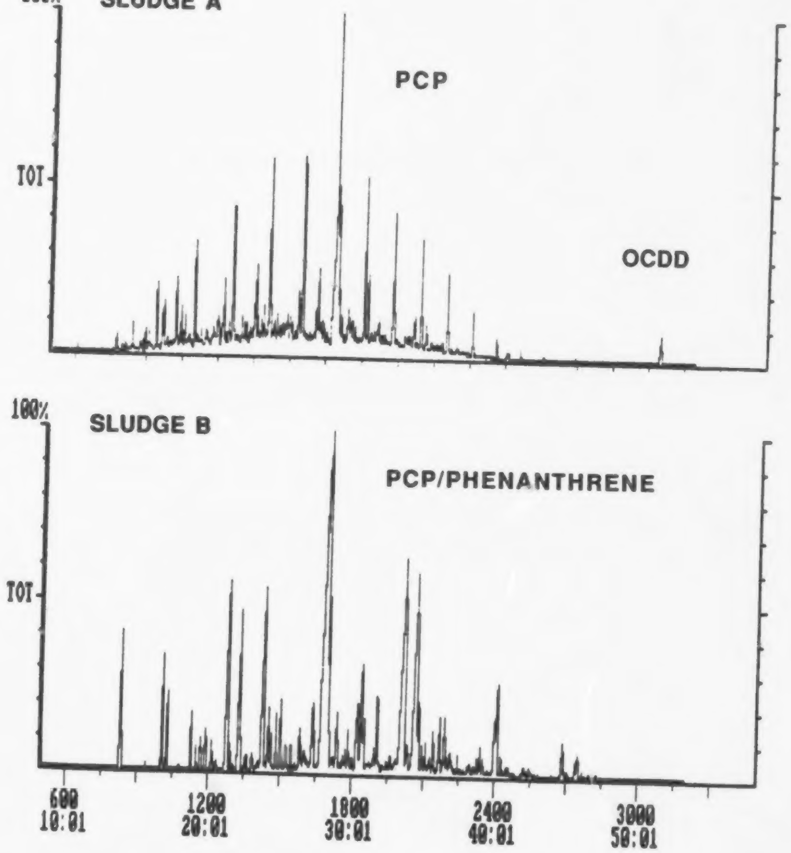

Figure 4 Pyran Level II analyses of sludge samples.

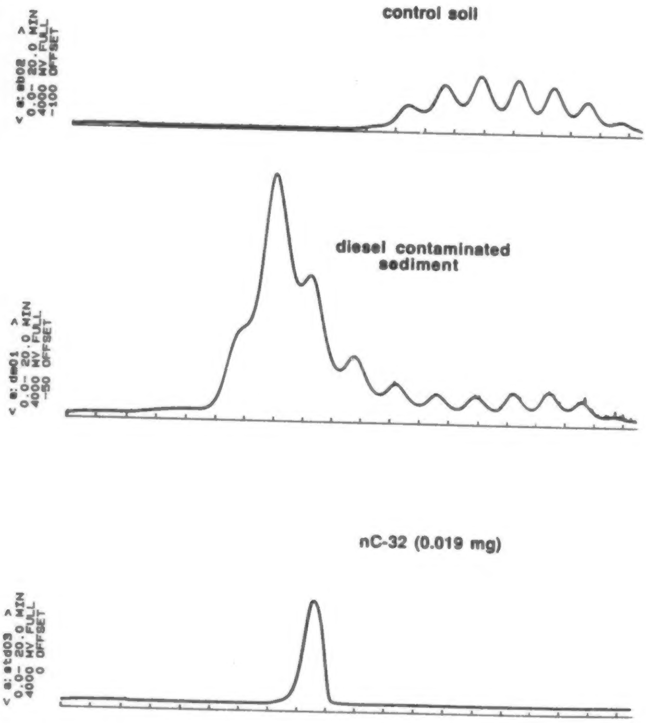

Figure 5 Level I thermal extraction profiles.

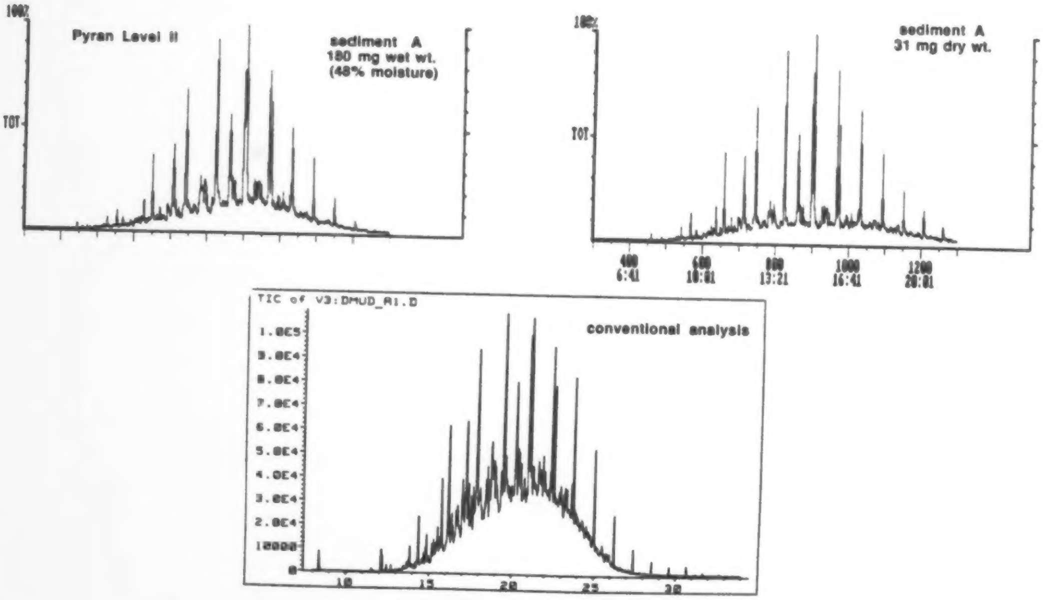

Figure 6 Comparison of Pyran to conventional analysis of sed. A.

Table 1 6-point Standard Curve

COMPOUND (AMW)	MEAN RT scan #	%RSD n=6	R
2-chlorophenol (128.6)	474.0	2.6750	0.91
1,4-dichlorobenzene (147.0)	506.8	2.5260	0.87
phenol (94.1)	508.8	2.4690	0.99
2-nitrophenol (139.1)	722.6	1.5330	0.88
2,4-dimethylphenol	803.8	1.6380	0.96
1,2,3-trichlorophenol (181.4)	811.0	1.5200	0.95
2,4-dichlorophenol (163.0)	812.7	1.6720	0.99
naphthalene (128.2)	819.0	1.6030	0.82
1,2,4-trichlorobenzene (181.4)	863.2	1.5640	0.97
4-chloro-3-methylphenol (142.6)	1019.0	1.2390	0.95
1,2,4,5-tetrachlorobenzene (216)	1050.7	1.1160	0.99
2,4,6-trichlorophenol (197.4)	1092.7	0.9984	0.98
acenaphthylene (152.2)	1221.0	0.7025	1.00
acenaphthene (154.2)	1278.5	0.8615	0.99
pentachlorobenzene (250.3)	1338.8	0.6398	1.00
fluorene (166.2)	1420.5	0.5749	0.82
hexachlorobenzene (284.8)	1596.8	0.4690	0.99
phenanthrene (178.2)	1658.0	0.3848	1.00
anthracene (178.2)	1682.0	0.3567	0.99
carbazole (167.2)	1733.8	0.2948	0.99
fluorenthrene (202.3)	1999.5	0.2163	0.99
pyrene	2050.8	0.1911	1.00
benz(a)anthracene (228)	2399.5	0.1079	0.98
chrysene (228)	2407.0	0.1084	0.99
benzo(a)pyrene (252)	2754.8	0.0741	0.98

Table 2

Comparison of Pyran Level II analyses of a diesel contaminated sediment to conventional solvent extraction-GC/MS analyses

PYRAN LV II	sample size mg dry wt.	nC-16 ng/mg	phytane ng/mg	nC-19 ng/mg	nC-20 ng/mg
wet sed.	(180) 94	74	53	35	28
dry sed. 1	42	58	43	45	40
dry sed. 2	35	95	58	58	45
dry sed. 3	20	95	53	63	53
dry sed. 4	31	100	89	63	51
MEAN		87.00	60.75	57.25	47.25
STDDEV		19.48	19.84	8.50	5.91
%RSD		22.39	32.66	14.85	12.51
CONV METH	g				
1a	5.90	92	48	61	61
1b	5.90	98	36	39	37
2a	5.89	120	56	64	60
2b	5.89	120	56	71	61
MEAN		107.50	49.00	58.75	54.75
STDDEV		14.64	9.45	13.82	11.84
%RSD		13.62	19.29	23.52	21.63

FIELD DEPLOYABLE INSTRUMENT FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS

E.B. Overton and C.B. Henry
#42 Atkinson Hall
Institute for Environmental Studies
Louisiana State University
Baton Rouge, LA 70803

C. Sutton
Ruska Instruments
P.O. Box 742688, Houston, TX 77274

Introduction

Chemical analyses play crucial roles in virtually all types of environmental chemical hazard assessments. For example, data used to determine if a site is contaminated with toxic chemicals are obtained from analysis of environmental samples taken from the site. The extent of contamination is determined from results of chemical analyses. The effectiveness of mitigative strategies can be determined from analytical data. Health effects may be determined from collaboration with chemical analysis data. Finally, legal claims of environmental contamination must be supported by indisputable data from chemical analyses.

There are standard methods and procedures such as those promulgated in SW846, which are designed to provide a recipe for chemical analyses of specific types of analytes in various sample matrices. Implicit in these promulgated procedures are techniques to ensure quality of the analytical results. All current methods are designed and intended for use in a conventional laboratory. Virtually no field screening methods for semivolatile organic analytes have been developed that do not require the services of a conventional trace chemical analysis laboratory. The types of conventional analytical procedures are outlined in Figure 1.

There are many applications where laboratory bound analytical procedures are not optimally suited. For example, site evaluation requires rapid turn-around of analytical results while personnel are deployed in the field. Also, excavation of contaminated material can be facilitated by rapid field screening analysis of samples. In this paper, we describe an analytical instrument that has potential to provide rapid field screening analyses of solid and semi-solid samples for semivolatile organic components.

Discussion

The Pyran Thermal Chromatograph, manufactured by Ruska Instruments of Houston, Texas, is an instrument that was specifically designed and developed to meet the analytical needs of petroleum exploration and development activities. It is a self-contained thermal extraction system and GCMS analyzer that is relatively compact, rugged and designed for field applications. It is constructed of quartz to provide the chemical inertness and stability that is needed for reproducible thermal extraction and pyrolysis of organic compounds from source rock samples. Since quartz does not absorb radiant energy, the quartz construction allows precise temperature control at both subambient and elevated temperatures using a computer controlled combination of cryogenic cooling (liquid CO_2) and radiant heating. The Level I analyzer includes a thermal extraction unit that is interfaced directly to a flame ionization detector (figure 2). The Level II unit includes a thermal extractor module that is interfaced, with all quartz components, to a specially designed capillary column gas chromatograph that has no moving parts (figure 3). Again, all quartz construction of the chromatographic oven and column allows precise and reproducible temperature control and programming from sub-ambient to several hundred degrees centigrade. The chromatographic effluents are detected by an Ion Trap Mass Spectrometer and analyzed by conventional data treatment software.

The Level I analyzer thermally extracts organic components and detects the substitutents without any chromatographic separation using flame ionization detection. **It is designed to permit rapid screening of samples and has analysis times of less than fifteen minutes.** The Level II analyzer has a thermal extraction module that is interfaced to a GCMS analyzer. The GCMS unit has the **capability to identify and quantitate specific substances that are thermally extracted from the sample**. Total analysis time, including extraction, is generally on the order of one hour. The Level II analyzer is designed to identify specific chemicals in a sample and to measure their concentrations with analytical turn-around times that are significantly faster than is available from conventional solvent extraction laboratory GCMS analysis of environmental samples. The thermal extraction procedure includes weighing a small aliquot of sample (10-100 mg) in an all quartz crucible. The crucible is then placed in the pyrocell compartment of

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the Pyran analyzer. The thermal extraction unit is then flushed with helium. If the sample is wet, it can be dried by raising its temperature to 60 to 80°C and venting the exhaust vapors prior to their entering the GCMS analyzer compartment. After drying (if needed), the sample temperature is raised rapidly to 250 to 300°C under precise temperature control. Sample analytes that have appreciable vapor pressures at 250 to 300°C are swept into the initial portion of a cryogenically cooled fused silica capillary column. The sample is then analyzed by conventional GCMS procedures. The drying and thermal extraction step takes between fifteen to twenty minutes. Figure 4 is an example of the temperature profiles of the pyrocell and GC columns during an analysis cycle.

Because the pyrocell's temperature can be precisely controlled at different set points, analytes with different vapor pressures can be selectively enhanced in the thermal extracts. This process has been called "thermal slicing." For example, if the pyrocell is heated to 175°C, the more volatile analytes will be driven out of the sample matrix and analyzed leaving unextracted those analytes that have extremely low vapor pressure at 175°C. Alternatively, more volatile analytes can be vented at 175°C and then the pyrocell's temperature raised to 250°C to enhance extraction of less volatile organic compounds. The precise control of the extracting conditions (temperature, helium flow rate, vent time and split ratios) provide a thermal extraction and analysis system with great flexibility.

The Pyran thermal extraction-GCMS analyzer is designed to analyze compounds that are in a solid or semi-solid sample matrix. Liquid or gaseous samples may be analyzed by passing the sample over some type of solid adsorbent, (tenax, activated carbon, XAD resin, etc.) and then thermally extracting the solid adsorbent with either a Level I or II Pyran analyzer.

It must be emphasized that thermal extraction removes all volatile components from the solid matrix not simply the analytes of interest. Special care must be exercised to identify and quantitate analytes of interest in the complex mixtures of organic matter that are routinely found in environmental the samples. Also, different types of solid materials have varying affinities for various types of analytes. A single thermal extraction sequence may not be suitable for the same analytes in different sample matrices. Examples of thermal extraction analyses are presented else where in these preceedings.

Conclusion

The Pyran Level I and II Analyzers have potential for valuable applications in many environmental analyses. Of particular importance is their application to the field screening for specific semi-volatile organic compounds in a variety of solid and semi-solid environmental samples. In addition to field screening analytical capability, these techniques have total analysis times of 60 to 90 minutes.

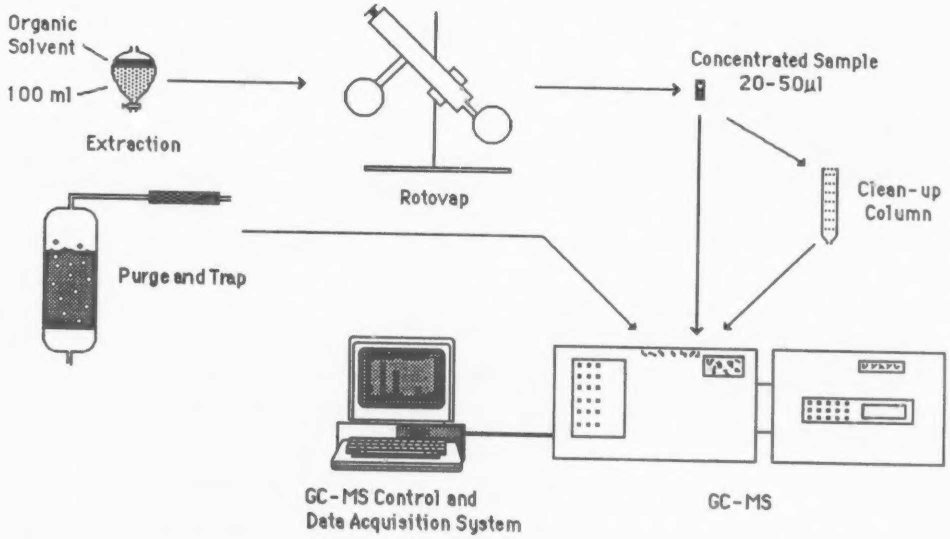

Figure 1. Conventional Laboratory Methods

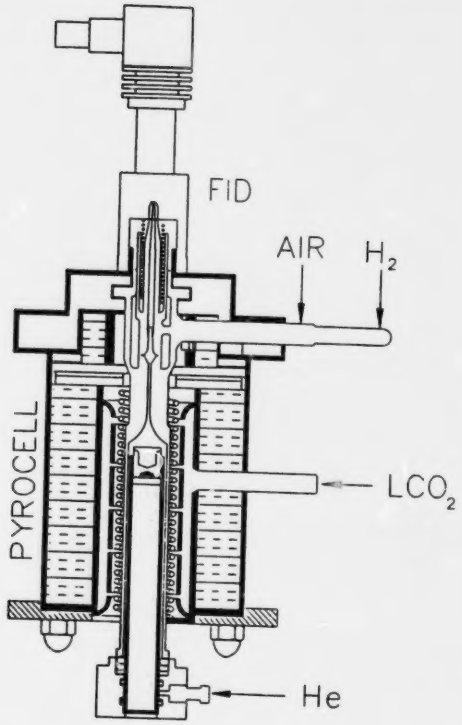
FID
AIR
H_2
PYROCELL
LCO_2
He

Figure 2. **Level I-FID analyzer schematic**

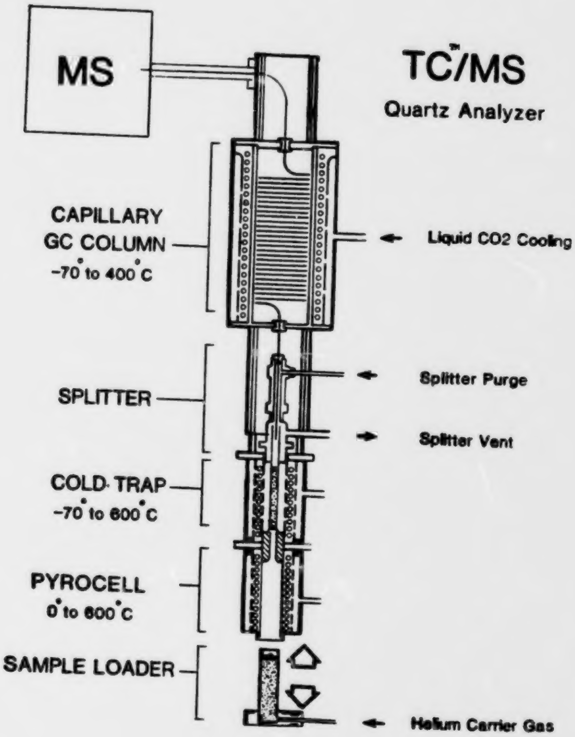
MS
TC/MS
Quartz Analyzer
CAPILLARY GC COLUMN
-70° to 400° C
Liquid CO2 Cooling
SPLITTER
Splitter Purge
Splitter Vent
COLD TRAP
-70° to 600° C
PYROCELL
0° to 600° C
SAMPLE LOADER
Helium Carrier Gas

Figure 3. **Level II-thermal extractor-MS analyzer schematic**

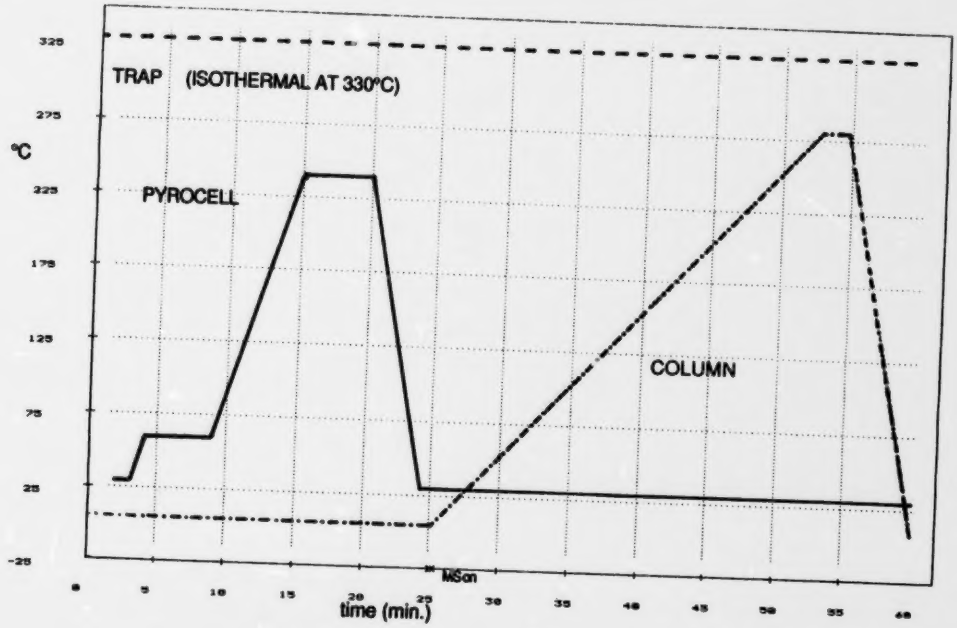

Figure 4. **Typical Pyran temperature program for wet sediments.**

EVALUATION OF MICROWAVE DETECTION TECHNIQUES TO PREPARE SOLID AND HAZARDOUS WASTE SAMPLES FOR ELEMENTAL ANALYSIS

Peter M. Grohse, David A. Binstock, and Alvia Gaskill, Jr., Research Triangle Institute, Research Triangle Park, North Carolina 27709; Howard M. Kingston, National Bureau of Standards, Gaithersburg, Maryland 20899; and Charles Sellers, Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC 20460

ABSTRACT

The techniques that are typically used to prepare Resource Conservation and Recovery Act (RCRA) wastes for analysis for metals and other elements are generally relatively time consuming, requiring several hours to several days to complete. They often involve the use of acid digestions and thermal decomposition steps which may result in analyte losses, incomplete recoveries, or sample contamination. These limitations are well known to the analytical community and to the end users of these data in the U.S. Environmental Protection Agency (EPA), States, and industry. The inefficiency of these techniques reduces laboratory sample throughput, drives up the cost of analytical testing, and impedes decisionmaking. Given these concerns, the hazardous waste industry and the EPA Office of Solid Waste Methods Section are interested in developing cost-effective sample preparation techniques for metals and other elements in environmental and process waste samples. Once developed, these techniques can then be written as methods for inclusion in EPA-OSW "Test Methods for Evaluation of Solid Waste SW-846" and made available to the user community.

This paper reports on the evaluation of several microwave assisted sample preparation methods for determining elements in solid waste. The method was evaluated for microwave-assisted digestion of sediments, sludges, soils, and oils.

INTRODUCTION

One particularly attractive sample preparation technique that is now receiving considerable attention is microwave-assisted sample dissolution. A typical example of this technique involves placing a sample in an acid solution in a closed inert vessel equipped with a pressure relief valve. The vessel is then subjected to microwave energy in a modified microwave oven. The conditions of high temperature generated in the container, coupled with the rapid heating of the sample via direct microwave energization of the acid molecules, can result in significantly reduced preparation time, from several hours in a conventional convection oven, hot plate, or steam bath to several minutes in the microwave oven.

Previously, work was reported on the evaluation of a commercially available microwave oven sample preparation system (Binstock et al., 1987). The effect of sample preparation conditions, including the acid matrix, heating time, and pressure, were evaluated for toxic or hazardous elements in particulates, ashes, oils, and oil fuels.

Based on in-vessel temperature and pressure profile studies conducted by the NBS, microwave oven preparation conditions for oils and soils have been determined and written as a draft method. These involve the use of concentrated nitric acid as the digestion medium. The intent is not to completely solubilize all elements in the sample. Rather, it is to solubilize those most likely to be made environmentally available.

NBS Standard Reference Materials, representative of oils and soils were prepared in this laboratory by several microwave-assisted digestion methods. Analyses were carried out by Inductively Coupled Plasma Spectrometry and Graphite Furnace Atomic Absorption.

EXPERIMENTAL METHODS

Microwave Oven

The MDS-81D Microwave system (CEM Corporation, Indian Trail, NC) was used for this study. The oven resembles a standard microwave oven, but is equipped with additional features to facilitate sample preparation. For example, the Teflon-coated microwave cavity has a variable speed corrosion resistant exhaust system and three safety interlocks. A precise microwave variable power supply is controlled by a programmable micro-processor digital computer. Other elements of the system include a rotating turntable, Teflon vessels with caps and a patented pressure relief valve, a capping system, and a cooling tank. The 120 m Teflon sample vessels and caps are designed to withstand pressures up to 100 psi and temperatures up to 200 °C.

Inductively Coupled Plasma Emission Spectrometry (ICPES)

Analytical measurements were performed using an Instrumentation Laboratory Plasma 200 ICP

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(Franklin, MA) or a Leeman Labs plasma Spec I ICP (Lowell, MA). Both instruments are sequential ICPs.

Atomic Absorption Spectrophotometry (AAS)

All AAS measurements were made using a Perkin Elmer Zeeman 3030 with graphite furnace atomization.

Reagents

All inorganic acids used were of "Ultrex" quality, from J. T. Baker Chemical Co. Other chemicals were of analytical reagent grade quality. Deionized (D.I.) water of 18 MΩ/cm specific resistivity was used.

Standard Reference Materials

The microwave method evaluation was carried out using the following materials:

- NBS SRM 4355—Peruvian Soil
- NBS SRM 2704—Buffalo River Sediment
- NBS SRM 1085—Wear Metals in Oil
- NBS SRM 1634b—Trace Elements in Fuel Oil.

In addition, to simulate a contaminated soil, a 1:1 mixture of 1634b and 2704 was prepared and analyzed.

Microwave Preparation Method

The method described below was developed for two vessels in the microwave oven and is optimized for temperatures and pressures that would produce efficient chemical decomposition of the sample. A higher power setting (574 W) would be utilized for six vessels.

A 0.25 g sample was heated in the microwave oven with 10 mL concentrated HNO_3 for ten minutes at a power setting of 344 watts. Two sample vessels at a time were placed in the microwave oven carousel with accompanying vapor trap vessels. Samples were diluted to 50 mL with D.I. water.

To reduce the likelihood of analyte loss due to volatilization, a configuration was employed which utilizes a second vessel to trap the hot acid vapor and any aerosol expelled when the pressure valve opens. A PFA Teflon tube connects the digestion vessel to a second vessel with a double-ported cap. The second port on the catch vessel remains open to the atmosphere preventing pressure buildup in the second vessel. The acid and any sample condensed in the second vessel are washed back into the sample vessel at the end of the microwave procedure and made to 50 mL volume with laboratory pure water. The contents of the sample vessel are then analyzed. Ten replicates of each of the four NBS SRMs, and the mixture, were digested and analyzed.

Samples were analyzed for 19 elements by ICP. As and Se were determined by graphite furnace AA.

Initially 0.5 g of Peruvian Soil was digested; however, this was found to cause undue pressure buildup and venting within the sample and overflow vessel. For subsequent runs, the sample weight was reduced to approximately 0.25 g. A tube was also added, connecting the overflow vessel with the center well on the carousel, to capture potential venting from the overflow vessel.

A study examining the overflow/capture solutions for any appreciable recoveries was performed. The condensate was collected and analyzed separately for four replicates each of Peruvian soil and wear metals in oil.

By comparison, a series of microwave digestions were performed that employed all reagents utilized in Method 3050 including nitric acid (HNO_3), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2). Samples that underwent these digestions included NBS 2704 (Buffalo River Sediment), the 1:1 mixture of NBS 2704 and NBS 1634b (Trace Elements in Fuel Oil), and NBS 1085 (Wear Metals in Lubricating Oils).

RESULTS

Since the microwave method is a non-rigorous acid-leach digestion (Tables 1, 2, and 3) like 3050, analytical results for the digestates of two soil/ sediment SRMs and the mixture were compared with those obtained using SW-846 method 3050.

In general, good agreement was obtained between the two methods. For most elements, comparative values were within 25 percent. Exceptions were Al and V in Peruvian Soil; Al, Ba, Be, and V in Buffalo River Sediment; and As and Be in the 1:1 mixture of Buffalo River Sediment and Fuel Oil. As predicted, using these non-rigorous digestions, the soil values were usually below the expected levels.

Graphite furnace analyses, for As and Se, were hindered by an apparent interference due to the high acid concentration of the digestate (approximately 20 percent). This was the apparent cause of a large erratic background signal.

Results for digestion of the two oil SRMs, along with analysis of spiked samples, are shown in Tables 4 through 7. In the case of SRM 1085, excellent agreement was obtained with the NBS Certified Values (Table 4), with all certified elemental concentrations within 14 percent of NBS values. SRM 1634b, Trace Elements in Fuel Oil, is a more difficult material because of increased viscosity, a larger amount of aromatic compounds, and lower elemental levels. Spike recoveries for both oil SRMs were excellent (Tables 6 and 7) with the exception of As and Se (see above).

An examination of the overflow/capture vessels for any appreciable elemental recoveries indicated that,with the exception of Zn in Peruvian soil, (with a mean condensate concentration of 6.4 µg/g) no recoveries above background level were observed for four replicates each of Peruvian Soil and Wear Metals in Oil. A small quantity of condensate was observed in four of the ten vessels.

For those samples undergoing the microwave digestion that utilized HCl and H_2O_2 in addition to HNO_3, results indicated that there was no apparent improvement over those results obtained with HNO_3 alone. Selected results are shown in Tables 8, 9, and 10.

CONCLUSIONS

Evaluation of a draft microwave digestion method, for determining elements in solid waste, indicates that the HNO_3 microwave method should prove a suitable alternative for SW-846 method 3050 with a substantial time/cost savings. It also provides satisfactory results for microwave digestion of oils.

Current studies are being conducted with the goal of optimizing sample weight and microwave power parameters. A collaborative study will then be conducted.

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TABLE 1. ICP ANALYSIS OF NBS SRM 4355 PERUVIAN SOIL[a]

Element	Mean ± S.D. (n=10)	3050 (n=3)	% Difference	IAEA values
Al	2.12 ± 0.20 %	3.34 ± 0.33	-36	8%
As	46.4 ± 1.5[b]	51.6 ± 3.5[b]	-10	90
Ba	140 ± 7	182 ± 17	-23	600
Be	0.758 ± 0.039	0.959 ± 0.059	-21	2
Cd	1.91 ± 1.01	ND[c]		2
Ca	10,500 ± 700	11,000 ± 900	-4.5	2%
Cr	13.7 ± 3.0	13.0 ± 1.6	+5.4	30
Co	10.6 ± 0.8	10.4 ± 1.2	+1.9	10
Cu	64.5 ± 2.0	60.3 ± 3.9	+7.0	80
Fe	2.40 ± 0.16 %	2.80 ± 0.24 %	-17	4%
Pb	131 ± 10	149 ± 9	-12	100
Mg	7,250 ± 300	7,480 ± 640	-3.1	2%
Mn	531 ± 20	565 ± 39	-6.0	900
Mo	ND[d]	ND[d]		2
Ni	10.1 ± 2.6	10.3 ± 2.0	-1.9	10
Se	ND[b,e]	ND[b,e]		1
Ag	ND[f]	ND[f]		2
Sr	85.3 ± 4.9	112 ± 9	-24	300
V	65.3 ± 4.3	93.0 ± 8.3	-30	20
Zn	396 ± 23	356 ± 30	+11	400

[a] Results in µg/g.

[b] Determined by GFAA.

[c] D.L. 1.0 µg/g.

[d] D.L. 2.75 µg/g.

[e] D.L. 0.2 µg/g.

[f] D.L. 3.0 µg/g.

TABLE 2. ICP ANALYSIS OF NBS 2704 BUFFALO RIVER SEDIMENT[a]

Element	Mean ± S.D. (n=10)	3050 (n=3)	% Difference
Al	1.25 ± 0.08 %	2.50 ± 0.19	-50
As	11.6 ± 0.5[b]	12.8 ± 1.1[b]	-9.4
Ba	79.3 ± 3.4	132 ± 10	-40
Be	0.689 ± 0.110	1.05 ± 0.05	-34
Cd	ND[c]	ND[c]	
Ca	187 ± 1.04 %	1.88 ± 0.01 %	-0.5
Cr	69.4 ± 3.4	78.9 ± 2.9	-9.5
Co	9.42 ± 1.26	10.8 ± 0.5	-13
Cu	89.1 ± 3.6	88.5 ± 1.7	+0.7
Fe	2.91 ± 0.11 %	3.29 ± 0.07 %	-12
Pb	153 ± 19	169 ± 8	-9.5
Mg	7,990 ± 240	9,080 ± 150	-12
Mn	465 ± 15	486 ± 4	-4.3
Mo	ND[d]	ND[d]	
Ni	37.8 ± 3.2	41.8 ± 0.6	-9.6
Se	ND[b,e]	ND[b,e]	
Ag	ND[f]	ND[f]	
Sr	30.9 ± 2.8	41.4 ± 1.0	-25
V	25.1 ± 1.5	49.4 ± 2.8	-49
Zn	392 ± 19	403 ± 4	-2.7

[a] Results in μg/g.

[b] Determined by GFAA.

[c] D.L. 1.0 μg/g.

[d] D.L. 2.75 μg/g.

[e] D.L. 0.2 μg/g.

[f] D.L. 3.0 μg/g.

TABLE 3. ICP ANALYSIS OF 1:1 MIXTURE: NBS 2704--BUFFALO RIVER SEDIMENT NBS 1634b--TRACE ELEMENTS IN FUEL OIL[a]

Element	Mean ± S.D. (n=10)	3050 (n=3)	% Difference
Al	6,550 ± 680	8,720 ± 1,760	-25
As	5.52 ± 0.32[b]	3.84 ± 0.99[b]	+44
Ba	45.7 ± 4.0	58.2 ± 8.0	-21
Be	0.741 ± 0.110	0.559 ± 0.053	+32.6
Cd	ND[c]	ND[c]	
Ca	1.04 ± 0.08 %	1.18 ± 0.04 %	-12
Cr	41.1 ± 13.8	45.1 ± 2.8	-8.9
Co	ND[c]	5.99 ± 0.29	
Cu	42.1 ± 5.6	51.6 ± 2.9	-18
Fe	1.40 ± 0.08 %	1.66 ± 0.09 %	-16
Pb	72.1 ± 13.4	83.4 ± 5.4	-14
Mg	4,000 ± 310	4,650 ± 250	-14
Mn	225 ± 16	252 ± 11	-11
Mo	ND[d]	ND[d]	
Ni	26.6 ± 5.6	35.4 ± 1.4	-25
Se	ND[b,e]	ND[b,e]	
Ag	ND[f]	ND[f]	
Sr	ND	15.1 ± 1.6	
V	41.5 ± 1.9	47.1 ± 5.0	-12
Zn	211 ± 18	231 ± 8	-8.6

[a] Results in µg/g.

[b] Determined by GFAA.

[c] D.L. 1.0 µg/g.

[d] D.L. 2.75 µg/g.

[e] D.L. 0.2 µg/g.

[f] D.L. 3.0 µg/g.

TABLE 4. ICP ANALYSIS OF NBS SRM 1085 WEAR METALS IN LUBRICATING OIL[a]

Element	Mean ± S.D. (n=10)	NBS values	% Difference
Al	337 ± 22	296	+14
As	b	---	
Ba	0.928 ± 0.890	---	
Be	ND[c]	---	
Cd	2.07 ± 0.92	---	
Ca	67.3 ± 91.6	---	
Cr	310 ± 10	298	+4
Co	ND[d]	---	
Cu	316 ± 11	295	+7
Fe	320 ± 11	300	+7
Pb	305 ± 19	(305)	0
Mg	300 ± 15	297	+1
Mn	0.837 ± 0.325	---	
Mo	265 ± 9	292	-9
Ni	310 ± 11	303	+2
Se	b	---	
Ag	309 ± 27	(291)	+6
Sr	ND[d]	---	
V	ND[e]	(<0.3)	
Zn	8.12 ± 4.89	---	

( ) Not certified

[a] Results in μg/g.

[b] To be determined by GFAA.

[c] D.L. 0.6 μg/g.

[d] D.L. 2.4 μg/g.

[e] D.L. 1.6 μg/g.

TABLE 5. ICP ANALYSIS OF NBS SRM 1634b TRACE ELEMENTS IN FUEL OIL[a]

Element	Mean ± S.D. (n=10)	NBS values
Al	29.7 ± 8.1	16
As	ND[b,c]	0.12
Ba	3.68 ± 0.36	(1.3)
Be	0.220 ± 0.023	---
Cd	ND[d]	---
Cr	ND[e]	(0.7)
Co	ND[f]	0.32
Cu	ND[g]	---
Fe	38.7 ± 4.4	31.6
Pb	ND[h]	(2.8)
Mg	13.7 ± 1.6	---
Mn	0.492 ± 0.224	0.23
Mo	ND[i]	---
Ni	29.3 ± 3.0	28
Se	ND[b,c]	0.18
Ag	ND[j]	---
Sr	ND[k]	---
V	57.7 ± 2.2	54.4
Zn	3.28 ± 3.69	3.0

( ) Not certified

[a] Results in µg/g.

[b] Determined by GFAA.

[c] D.L. 0.4 µg/g.

[d] D.L. 0.9 µg/g.

[e] D.L. 0.6 µg/g.

[f] D.L. 2.4 µg/g.

[g] D.L. 3.6 µg/g.

[h] D.L. 9.2 µg/g.

[i] D.L. 10.0 µg/g.

[j] D.L. 4.8 µg/g.

[k] D.L. 3.0 µg/g.

TABLE 6. ICP ANALYSIS OF SPIKED NBS OILS SRM 1085--WEAR METALS IN LUBRICATING OIL[a]

Element	Expec.	Found	% Rec.	Unspiked concentration
Al	2.00	1.91	96	1.47
As	0.200	0.121[b]	60	ND
Ba	2.00	1.90	95	0.004
Be	2.00	1.93	96	ND
Cd	2.00	1.85	92	0.009
Ca	2.00	1.74	87	0.293
Cr	2.00	1.84	92	1.35
Co	2.00	1.93	96	ND
Cu	2.00	1.86	93	1.38
Fe	2.00	2.00	100	1.40
Pb	2.00	1.85	92	1.33
Mg	2.00	1.83	92	1.31
Mn	2.00	1.97	98	0.004
Ni	2.00	1.80	90	1.35
Se	0.200	0.120[b]	60	ND
Ag		[c]		
Sr	2.00	1.97	98	ND
V	2.00	1.94	97	ND
Zn	2.00	1.86	93	0.005

[a] Results in $\mu g/mL$.

[b] Determined by GFAA.

[c] Spike unsuccessful.

TABLE 7. ICP ANALYSIS OF SPIKED NBS OILS SRM 1634b--FUEL OIL[a]

Element	Expec.	Found	% Rec.	Unspiked concentration
Al	2.00	2.06	103	0.127
As		b		
Ba	2.00	1.84	92	0.016
Be	2.00	1.87	94	0.001
Cd	2.00	1.82	91	ND
Ca	2.00	1.77	88	0.364
Cr	2.00	1.89	94	0.011
Co	2.00	1.92	96	ND
Cu	2.00	1.88	94	ND
Fe	2.00	2.05	102	0.166
Pb	2.00	1.87	94	ND
Mg	2.00	1.90	95	0.059
Mn	2.00	1.94	97	0.002
Mo	2.00	1.77	88	ND
Ni	2.00	1.92	96	0.126
Se		b		
Ag		c		
Sr	2.00	2.02	101	ND
V	2.00	1.94	97	0.247
Zn	2.00	1.84	92	ND

[a] Results in μg/mL.

[b] Not spiked.

[c] Spike unsuccessful.

TABLE 8. ICP ANALYSIS OF NBS 2704 BUFFALO RIVER SEDIMENT[a]

Element	HNO_3 Mean ± S.D. (n=10)	$HNO_3/HCl/H_2O_2$ Mean ± S.D. (n=5)	3050 (n=3)	NBS Values
Al	1.25 ± 0.08 %	1.59 ± 0.18 %	2.50 ± 0.19 %	6.11 %
Ba	79.3 ± 3.4	117 ± 9	132 ± 10	414
Be	0.689 ± 0.110	0.634 ± 0.052	1.05 ± 0.05	---
Cd	<0.9	2.57 ± 0.32	<0.9	3.45
Ca	1.87 ± 1.04 %	2.09 ± 0.10 %	1.88 ± 0.01 %	2.60 %
Cr	69.4 ± 3.4	103 ± 6	78.9 ± 2.9	135
Co	9.42 ± 1.26	8.68 ± 1.00	10.8 ± 0.5	14.0
Cu	89.1 ± 3.6	110 ± 2	88.5 ± 1.7	98.6
Fe	2.91 ± 0.11 %	2.96 ± 0.10 %	3.29 ± 0.07 %	4.11 %
Pb	153 ± 19	133 ± 12	169 ± 8	161
Mg	7,990 ± 240	8,990 ± 360	9,080 ± 150	1.20 %
Mn	465 ± 15	478 ± 12	486 ± 4	555
Ni	37.8 ± 3.2	41.3 ± 3.6	41.8 ± 0.6	44.1
Sr	30.9 ± 2.8	41.7 ± 3.6	41.4 ± 1.0	(130)
V	25.1 ± 1.5	30.4 ± 4.2	49.4 ± 2.8	95
Zn	392 ± 19	432 ± 49	403 ± 4	438

[a]Results in μg/g.

TABLE 9. ICP ANALYSIS OF 1:1 MIXTURE: NBS 2704--BUFFALO RIVER SEDIMENT NBS 1634B--TRACE ELEMENTS IN FUEL OIL[a]

Element	HNO_3 Mean ± S.D. (n=10)	$HNO_3/HCl/H_2O_2$ Mean ± S.D. (n=5)	3050 (n=3)
Al	6,550 ± 680	6,510 ± 2,380	8,720 ± 760
Ba	45.7 ± 4.0	55.5 ± 13.6	58.2 ± 8.0
Be	0.741 ± 0.110	0.197 ± 0.069	0.559 ± 0.053
Cd	<0.9	1.29 ± 0.53	<0.9
Ca	1.04 ± 0.08 %	0.864 ± 0.047 %	1.18 ± 1.04 %
Cr	41.1 ± 13.8	43.6 ± 3.5	45.1 ± 2.8
Co	<1.0	3.95 ± 0.32	5.99 ± 0.29
Cu	42.1 ± 5.6	44.2 ± 3.6	51.6 ± 2.9
Fe	1.40 ± 0.08 %	1.18 ± 0.07 %	1.66 ± 0.09 %
Pb	72.1 ± 13.4	56.0 ± 4.9	83.4 ± 5.4
Mg	4,000 ± 310	3,570 ± 320	4,650 ± 250
Mn	225 ± 16	184 ± 9	252 ± 11
Ni	26.6 ± 5.6	27.4 ± 0.7	35.4 ± 1.4
Sr	<2.4	22.8 ± 5.8	15.1 ± 1.6
V	41.5 ± 1.9	32.1 ± 4.9	47.1 ± 5.0
Zn	211 ± 18	148 ± 8	231 ± 8

[a]Results in μg/g.

TABLE 10. ICP ANALYSIS OF NBS SRM 1085 WEAR METALS IN LUBRICATING OILS[a]

Element	HNO_3 Mean ± S.D. (n=10)	$HNO_3/HCl/H_2O_2$ Mean ± S.D. (n=5)	NBS Values
Al	337 ± 22	239 ± 17	296
Ba	0.928 ± 0.890	0.250 ± 0.153	---
Be	<0.6	<0.6	---
Cd	2.07 ± 0.92	<0.9	---
Ca	67.3 ± 91.6	37.8 ± 16.4	---
Cr	310 ± 10	275 ± 17	298
Co	<2.4	<2.4	---
Cu	316 ± 11	229 ± 14	295
Fe	320 ± 11	250 ± 12	300
Pb	305 ± 19	209 ± 18	(305)
Mg	300 ± 15	196 ± 16	297
Mn	0.837 ± 0.325	1.20 ± 0.16	---
Mo	265 ± 9	168 ± 15	292
Ni	310 ± 11	237 ± 9	303
Ag	309 ± 27	76.2 ± 78.0	(291)
Sr	<2.4	<2.4	---
V	<1.6	<1.6	(<0.3)
Zn	8.12 ± 4.89	9.06 ± 1.53	---

( ) Not certified.

[a] Results in μg/g.

Rapid Screening of Organic Contaminants Using a Mobile Mass Spectrometer in the Field

Michael C. Hadka, Ph.D.
Walter B. Satterthwaite, Assoc.
720 N. Five Points Road
West Chester, Pa. 19380

Randall K. Dickinson, PG.
United Engineers
30 S. Seventeenth St.
Philadelphia, Pa. 19103

ABSTRACT

The source of organic contaminants emanating from a landfill were determined by on–site screening using a mobile mass spectrometer (MM–1). The rapid screening provided by the MM–1 was an effective tool in providing immediate sample analysis for quick response and decision making in the field. In addition, positive identification of the contaminants was obtained from the mass spectra provided by the instrument. The MM–1 was used to screen soil, soil gas, and ground water for volatile organics down to the 10 ppb level with an analysis time of ten seconds.

Volatile chlorinated organics were discovered in water from a storm sewer located beneath a landfill which was used to dispose of incinerator ash. Water in the storm sewer was first screened by the MM–1 and the source was isolated. Contaminated water was leaking into the joints of one 6' section of the sewer. A grid pattern was laid out and the contamination was delineated by obtaining continuous split spoon soil samples with immediate analysis by the MM–1. The MM–1 data was plotted on the sampling grid pattern, thus delineating the source location.

Compounds identified by the MM–1 include 1,1,1–trichloroethane, trichloroethene and dichloroethenes. Selected samples sent to a laboratory verified the MM–1 results.

INTRODUCTION

Rapid on–site analysis is the most economical method for site investigations. It allows the problem to be defined in the field instead of waiting for laboratory analysis in order to determine the site condition. For organic analysis, on–site analytical techniques usually involve photoionization detectors, portable gas chromatographs or a mobile laboratory in a trailer. This equipment is either low in sensitivity, poor in selectivity, or expensive to set up and operate.

As an innovative approach to rapid on–site analysis, a mobile mass spectrometer was used during an on–site investigation to pin point the source of contamination and delineate the contaminant plume in soil and water. The mobile mass spectrometer was chosen for its high sensitivity, unambiguous identification, high dynamic range, freedom from interferences, and ruggedness. The instrument provided rapid identification of the contaminant(s) and semi–quantitative results which facilitated the field scientists' ability to make on the spot decisions to determine the next step of the investigation. This procedure resulted in a more thorough site investigation while at the same time completing the job in days instead of weeks.

INSTRUMENTATION

The instrumentation used consisted of a battery operated mobile mass spectrometer (MM–1) manufactured by Bruker Instruments and mounted in a four wheel drive vehicle (Figure 1). The three main sections of the instrument are the sample inlet system, the quadrupole mass spectrometer and the monitor. The sample inlet system is the most unique feature of the instrument, allowing the direct sampling of air, water, and solids with little to no sample preparation.

The sample inlet system consists of a 3.5 meter fused silica column inside a flexible hose (Figure 2). One end of the sample inlet system is connected to the mass spectrometer. A large silicone membrane is attached to the sampling end of the inlet system. Organic vapors in the air are continuously drawn through the heated silicone membrane and capillary column with a suction pump and into the mass spectrometer.

The instrument can be run in one of two modes. In the first mode the sample inlet system is operated isothermally, up to 230 C. In the second mode the sample inlet is operated in a temperature program mode allowing the temperature to be ramped from a low temperature to a higher temperature. The temperature program mode allows a limited separation of the compounds by the capillary column.

Compound identification is performed by one of two methods. The first method uses a selected ion monitoring procedure for specified target compounds. Up to four ions per compound and up to 22 organic compounds can be monitored simultaneously. In this mode the instrument's

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microprocessor identifies each compound by determining if the monitored ions are above a minimum detection level and their relative intensities matches the library reference. The monitor displays the intensity of the ions monitored for each compound and what compounds were identified. The second method of identification is performed by acquisition of the full spectrum (up to mass 400). The instrument's library is searched for a match and the name of the compound is displayed if a match is found. If no match is found the spectrum can be interpreted and the compound identified by a mass spectroscopist/chemist.

The intensities of the ions are proportional to the compound's concentration. The ion intensity for each compound identified is displayed on the monitor as a log function. Thus, every increase in one log unit is a tenfold increase in concentration. Calibration of the instrument is performed by using standards of known concentration. The instrument is capable of measuring up to eight orders of magnitude from 10 parts per billion (ppb) in air or water, up to the percent range. The detection limit for soils is around 100 ppb. Compound identification and quantification can be performed in five to ten seconds.

ANALYTICAL METHODOLOGY

At the beginning of each day the instrument is calibrated and background concentrations are obtained. The mass calibration is performed automatically by the instrument using a fluorohydrocarbon (FC–77) standard. A background is taken by sampling the air in a clean environment. The instrument automatically sets the minimum detection limit during the background acquisition. During the operation the instrument uses argon in the air as an internal standard to continuously monitor the performance of the mass spectrometer. The capillary column and silicone membrane are set to operate at 180 degrees C. After setup and preparation, the instrument is driven to each sample location.

Sampling is done directly using the sample inlet system with little or no sample preparation. With the instrument's mobility and the 3.5 meter reach of the sample inlet system, most samples can be measured in–situ by one of the following procedures:

o For soil and solids, the heated sample probe is pressed against the sample. Volatiles and semivolatiles are heated and vaporized into the sample inlet system. Thus even PCBs can be analyzed directly by the MM–1.

o For aqueous samples, a headspace technique is used. The sample is collected in a 500 ml wide–mouth bottle allowing a 4 cm headspace below the lid. The bottle is sealed and shaken. The lid is removed and the sample probe immediately placed over the mouth of the bottle.

o For soil gas samples the probe is inserted down the hole of the soil boring.

For this work soil gas, soil and aqueous samples were measured. The soil was analyzed on the surface and at various depths from samples collected in 2 inch diameter split spoons.

SITE BACKGROUND

The site investigation was performed at a municipal landfill in eastern New York. The landfill is roughly rectangular in shape with the long axis oriented north–south. The total filled area encompasses approximately 26 acres. Since its inception in the 1930's, the facility has been operated by the local city public works authority. According to available records, no private haulers or disposal companies have ever used the landfill.

Originally, the landfill was used for the disposal of ash residue from the city operated sanitary waste incinerator. Since the termination of incineration operations in the late 1970's, the landfill has been used for the composting of leaves and grass cuttings which continues to the present time. The leaves and cuttings are shredded, mixed with silty sand, and sold as topsoil substitute.

The ash material varies in depth from 9 to 18 feet and is grayish–black to black similar in nature to silt and sandy silt. Bulk material such as wood, carpeting, and tires were disposed of along with the ash and during the site investigation were found sporadically throughout the deposit. A greenish–gray clay underlies the ash material and is the uppermost naturally occurring deposit at the site. The clay layer is 20 feet thick at the northwestern end of the landfill, gradually pinching out, and is not present in the southeastern portion of the landfill. The clay overlies the Manhattan Formation which consists of a mica rich, schistose gneiss underlying the entire area of the landfill. Locally, the upper portion of the bedrock may be highly weathered to essentially a platy, fine to medium grained sand. The weathered portion may be up to 10 feet in thickness.

In 1984 and 1985, several storm sewer and sanitary sewer pipelines were constructed across the landfill (Figure 3). The storm sewer lines drained surface water runoff from a residential area on the west side of the landfill. The runoff water was discharged to an unnamed stream that formed the west border of the landfill. The pipelines were installed at least several feet below the bottom of the ash fill. In some areas, channels were excavated in the bedrock to lay the pipelines where competent rock was encountered.

In August and October of 1986 and March 1987 the local environmental agency in conjunction with the state environmental agency sampled and analyzed several of the storm sewer lines that traverse the landfill. Samples were obtained from the manhole inlets along the pipelines and the discharge outlets to the stream. Sample analyses indicated the presence of chlorinated solvents. Table 1 is a summary of the sample analytical results, and sample locations are shown on Figure 3. The principal compounds identified were 1,1,1–trichloroethane, 1,1–dichloroethane, 1,1–dichloroethene, 1,2–dichloroethenes, trichloroethene, and vinyl chloride. The greatest concentration encountered was 4600 ug/l (ppb) for 1,1,1-trichloroethane.

PHASE I - SITE SCREENING

The initial phase of the investigation was to verify the presence of contaminants at the locations sampled by the agencies. The two pipelines that traversed the southern portion of the landfill were sampled and analyzed with the MM-1. Samples of the water in the pipelines were obtained from the manhole inlets. Additionally, the pipeline outfalls to the stream as well as sections of the stream were sampled and analyzed. The results of these analyses are shown on Table 2.

The analyses indicated that the contamination was emanating from the southernmost pipeline. The sample locations are shown on Figure 3. The contaminants were encountered at the greatest concentration in manhole (MH) 11. The same contaminants were detected at a lesser concentration at the outfall of the MH-11 pipeline and in the stream, downstream of the same outfall.

PHASE II - CONTAMINANT LOCATION

Phase I of the investigation indicated that the contamination was entering the pipeline somewhere between MH-10 and MH-11. Assuming a point source, Phase II was to determine the exact location of the contamination along the pipeline.

This section of the pipeline was constructed of precast, 3-foot inside diameter, reinforced concrete, sectioned in 6 foot lengths. Each section was fitted with a rubber gasket at the connection ends.

Based upon discussions with municipal department employees, this section of the pipeline was located beneath the ground water table. This was a localized condition because of an adjacent area to the pipeline which was formerly used as a drainage basin for surface runoff within the landfill. Consequently, the pipeline was inspected from the inside where three joints were found to be leaking from the top. The analyses of these samples did not detect any contaminants.

Further discussions with the landfill operators revealed that some small amount of liquids of unknown origin were once disposed of in the former drainage basin.

Three test pits were excavated in the former drainage basin adjacent to the pipeline (see Figure 3). The pits were excavated to a depth of approximately 8 feet. Standing water in the pits was approximately three feet below the ground surface. Several samples were obtained from each pit but none of the chlorinated organics compounds were detected by the MM-1.

At this point, the pipeline was investigated once again. A water sample was obtained immediately down flow of each section joint. Every sample was analyzed by the MM-1. Starting at MH-10, twelve of the joints downstream of the manhole were sampled and tested negative for the chlorinated organic compounds. The pipe joints upstream of MH-11 were sampled and tested. The third pipe joint upstream from MH-11 was analyzed with the greatest concentration (3000 ppb). The fourth joint upstream of the manhole encountered chlorinated organic compounds at the limit of detection (see Table 3). The location where the contaminants were entering the pipeline was 18 feet upstream from manhole MH-11.

PHASE III - SOURCE DELINEATION

As an initial attempt to locate the contaminant source, a test pit was excavated down to the storm sewer line at the joint located in Phase II. The excavation pit indicated that the bedrock was removed to create a channel for the pipeline in this section of the line. The 3-foot pipeline was located approximately 13 feet below the ground surface and the ground water was approximately 15 feet below the surface.

Soil and water samples were obtained from the pit and analyzed indicating elevated concentrations of chlorinated organics. The greatest concentrations detected were up to 500,000 ug/L.

The highest contamination was encountered in a tan colored sand deposit that apparently was oriented nearly perpendicular to the pipeline and approximately eight feet below the ground surface.

This deposit was saturated and was draining into the excavated pit. The sand provided a conduit for the contaminated water which drained into and collected in the channel excavated in the bedrock. The water then was entering the pipeline at one of the joints which was improperly sealed. The competent bedrock was relatively impermeable which precluded the vertical migration of the contaminated water.

A 50 foot by 50 foot borehole grid pattern (Figure 4) was laid out in the area most likely to contain the source of the contamination. Grid point B1 was the location where the contamination was entering the pipeline. Soil borings were drilled at each coordinate location. Soil samples were obtained using continuous split-spoon samplers. Each sample was immediately analyzed by the MM-1 to determine the presence of volatile organic compounds. Each boring was completed to auger refusal at the top of competent bedrock. Soil samples could not be recovered from a number of sampling intervals because of subsurface conditions encountered. Wood, tires, and the localized very loose, non-cohesive nature of the ash material prevented recovery of samples in several of the split spoons samples.

The sequence of drilling on the grid pattern was dictated by the results of the boring sample analysis by the MM-1 as each boring was completed. Once the approximate location of the source had been determined, additional boreholes were drilled off the grid pattern to further delineate the source of the contamination. As shown on Figure 5, the area of the contamination is limited to that encompassed by a diagonal from coordinate B1 to C2, extending slightly beyond the C2-B2 gridline, and southward to the B gridline.

Figure 6 is a fence diagram depicting the borehole locations, corresponding depth with analytical results. As can be seen from the figure, the contaminated area varied in depth from between 10 to 16 feet below the ground surface and was up to 6 feet thick. Based on the analytical results, the source extended approximately 80 feet in a northeast direction from the pipeline and was roughly 20 feet wide. Assuming these dimensions, the volume of the contaminated area was 360 cubic yards of soil/fill material.

VERIFICATION OF MM–1 RESULTS

In order to verify the MM–1 results a select number of samples were sent to a certified laboratory for volatile organic analysis. The samples were analyzed using the EPA Contract Laboratory Program (CLP) procedures utilizing gas chromatography/mass spectroscopy. To minimize the loss of volatiles from the soil the CLP procedure was modified by collecting the sample in bottles containing a known volume of methanol. Thus the methanol served as a preservative and an extraction solvent for the volatiles. Methanol is the extraction solvent used in the CLP procedure.

The results for the soil verification samples, Table 4, confirm the identifications of dichloroethenes, 1,1,1–trichloroethane and trichloroethene by the MM–1. The MM–1 could not distinguish the differences between 1,1–dichloroethene and 1,2–dichloroethene in the operation mode used. The MM–1 did not detect low levels of 1,1–dichloroethane and 1,1,2,2–tetrachloroethane.

Since the ion intensity is directly proportional to the concentration, the log ion intensity from the MM–1 can be used to calculate semiquantitative results. The laboratory results for the soil samples are compared to the MM–1 output in Table 4 and plotted in Figure 7. This plot was used to estimate the concentration of the organics for each sample. Since the greatest variable in measurement is the sample size, the log–log plot in Figure 7 is sufficient to estimate semiquantitative results. For soil samples when the sample probe is pressed against the sample such factors as packing density of the soil and the depth to which the organics are stripped effects the results by this technique.

In the ground water matrix, shown in Table 5, the results of verification samples show agreement with the MM–1 results. Vinyl chloride and 1,1–dichloroethane were not detected in Sample 3 by the MM–1 due to interference from other chlorinated organics present. This is because in the isothermal mode, all of the compounds are detected at once and the ions monitored for vinyl chloride and 1,1–dichloroethane are common to the other chlorinated compounds.

COST COMPARISON

Table 6 is a cost summarization for the three phases of work that were completed for the site investigation. The actual costs incurred using the MM–1 are compared with the estimated costs expected if the investigation was conducted using standard EPA protocol (1). The actual costs for the field work were $52,400 as compared to an estimated cost of $248,000 using EPA procedures. The laboratory costs were calculated based on the analysis of the number of samples obtained during the actual investigation. Travel expenses were considered to be equivalent even though the EPA procedure would be of longer duration and, therefore, more costly.

In addition to the lower costs, the other advantages of utilizing the mobile mass spectrometer include the following:

o Instantaneous results confined the extent of the study area to just that which was contaminated. Every sample analyzed continually defined the limit of contamination as the field work progressed. This subsequently reduced the number of samples required as compared to having all the samples laboratory analyzed.

o The MM–1 was used as an air monitor for personnel health and safety during field operations. The air monitoring results were used as the trigger to upgrade personal protective clothing and equipment. A higher work productivity was achieved using this procedure than if a defined level of protection would have been required to be worn at all times during the field work. The air monitoring capabilities of the MM–1 not only identified conditions when upgraded levels of personnel protection were required but also provided approximate contaminant concentrations to determine the specific level of protection.

o The most significant advantage using the MM–1 is time. The actual project was completed four and one–half weeks including oral presentation of the data and final written report submittal to the agencies. Under EPA protocol, a minimum of 4 to 6 weeks would be required after each phase of work before the analytical data could be obtained from the laboratory. Consequently, the project would be estimated to be completed in 16 to 22 weeks using standard EPA procedures.

o The necessary manpower is reduced since only a minimum number of samples are analyzed by a laboratory. Bottle preparation, sample handling, chain of custody, sample logs, decontamination procedures and shipping of the samples are drastically reduced.

These items are indirect cost factors which were not incorporated into the calculations detailed on Table 6. Therefore, the estimated cost of $248,000 to complete the EPA conducted investigation is conservative.

CONCLUSION

The use of the MM–1 for the site investigation provided a cost effective method to accurately analyze environmental samples in the field. Positive identification of the organic contaminants present and their concentrations was provided to the investigating team on a sample by sample basis. This allowed site personnel to make immediate judgments as to where to sample next and quickly determine the source of the contamination and delineate the contaminant plume. With the rapid turnaround afforded by the MM–1, less time was spent at the site for manpower and equipment while at the same time keeping laboratory costs minimal. Thus, costs of the investigation were only one–fifth of a conventional investigation. Significantly more samples may be tested using this technique than would be with a conventional investigation. In addition, the sampling crew was not randomly sampling the site and sending unnecessary samples to the laboratory, increasing costs.

As a field investigating tool the MM–1 is extremely versatile; capable of testing air, water and soil with little or no sample preparation. Its sensitivity is better than most field equipment and it gives positive compound identification that most field equipment is not capable of doing. Although the MM–1 did not identify every compound present in the operation mode used, the MM–1 was able to identify the major contaminants and solve the problem in the field. If the identification of additional compounds is required gas chromatography separation is available with the sample probe by using temperature programming.

The MM–1 also serves as a valuable quality assurance tool. Since it measures most samples either in–situ or immediately thereafter, the MM–1 can be used to verify laboratory results which are prone to errors due to cross–contamination, loss of volatiles during transport of the samples, or internal laboratory contamination during sample preparation and analysis.

References

1. U.S. Environmental Protection Agency "Remedial Action Costing Procedures Manual" EPA/600/8–87/049, October 1987

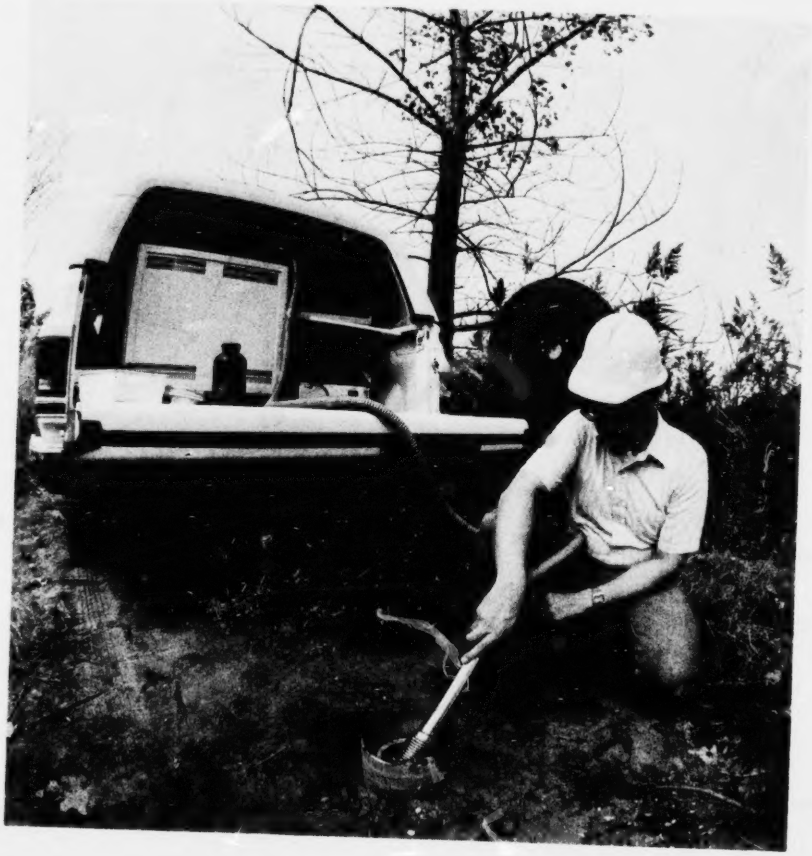


Figure 1. MM-1 mounted in a four wheel drive vehicle with the sampling inlet system used to measure the headspace of a well.

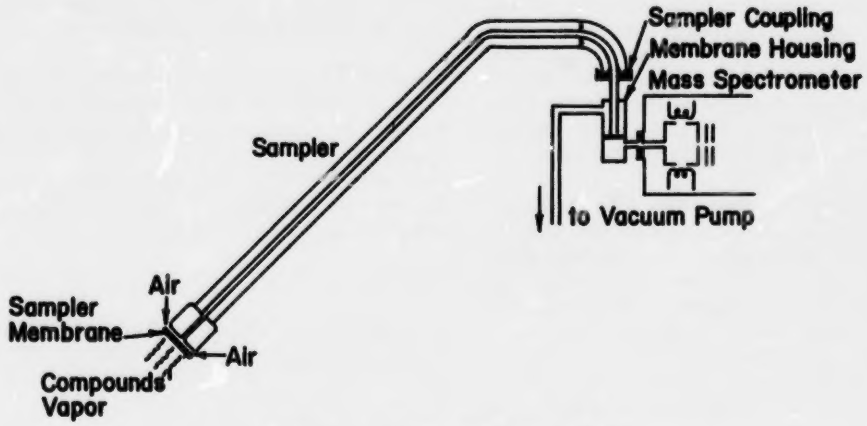

Sampler Coupling
Membrane Housing
Mass Spectrometer
Sampler
to Vacuum Pump
Air
Sampler
Membrane
Air
Compounds
Vapor

Figure 2 - Diagram of Sample Probe

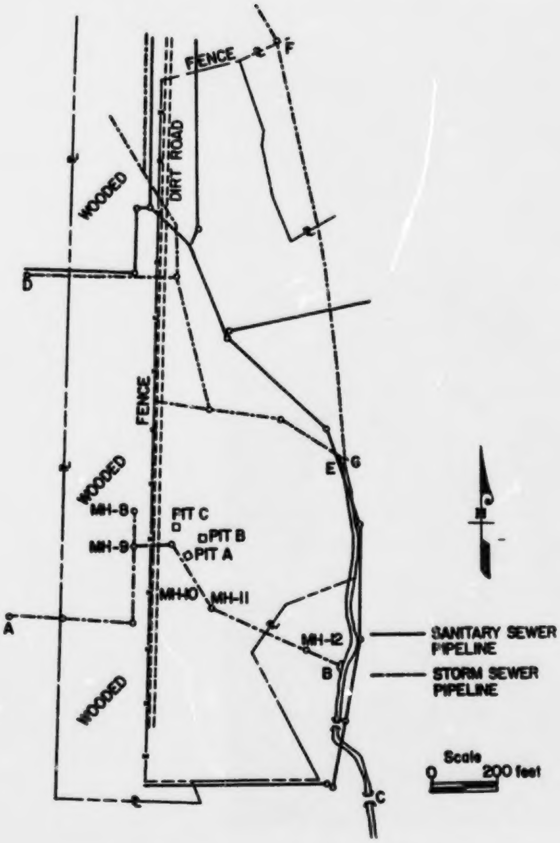
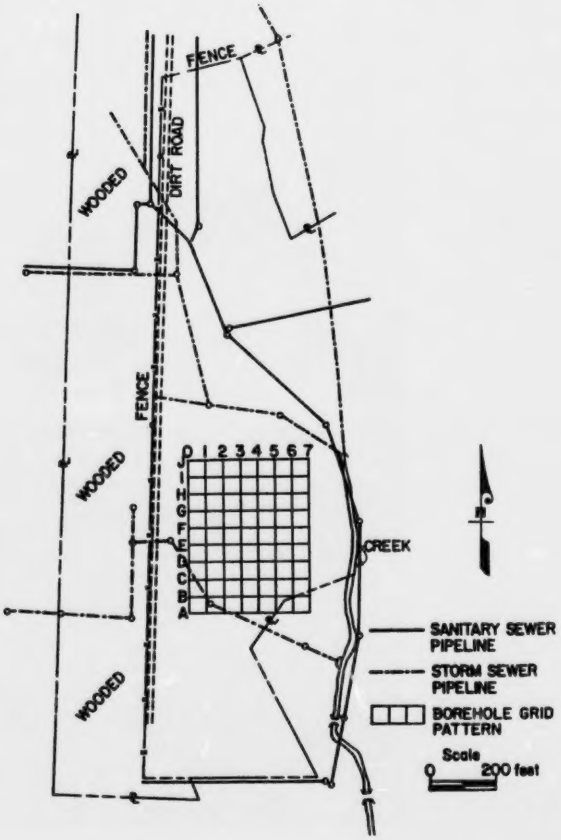

FENCE
F
WOODED
DIRT ROAD
D
FENCE
E
G
WOODED
MH-8
PIT C
PIT B
MH-9
PIT A
MH-10
MH-11
A
MH-12
B
SANITARY SEWER PIPELINE
STORM SEWER PIPELINE
WOODED
Scale
0
200 feet
C
N

Figure 3 - Storm Sampling and Test Pit Locations


FENCE
WOODED
DIRT ROAD
FENCE
0 1 2 3 4 5 6 7
J
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H
G
F
E
D
C
B
A
WOODED
CREEK
SANITARY SEWER PIPELINE
STORM SEWER PIPELINE
BOREHOLE GRID PATTERN
WOODED
Scale
0
200 feet
N

Figure 4 - Location of Grid Pattern for Drilling

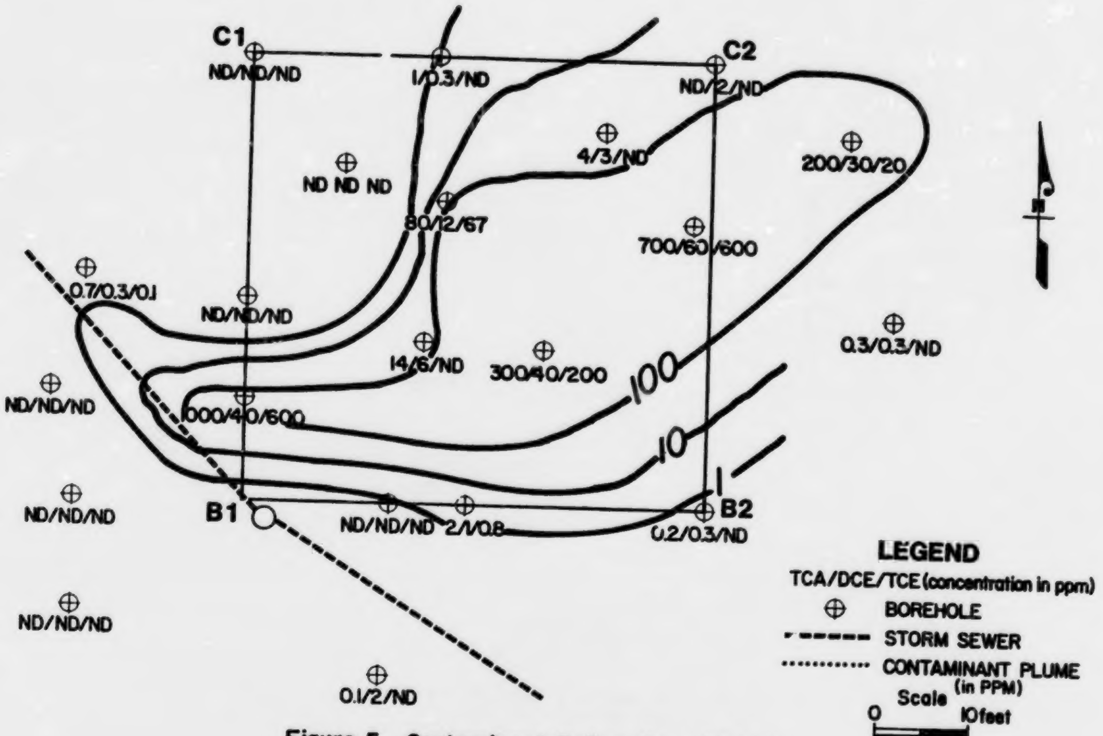
C1
C2
B1
B2
ND/ND/ND
1/0.3/ND
ND/2/ND
4/3/ND
200/30/20
ND ND ND
80/12/67
700/60/600
0.7/0.3/0.1
ND/ND/ND
14/6/ND
300/40/200
0.3/0.3/ND
100
ND/ND/ND
1000/40/600
10
1
ND/ND/ND
ND/ND/ND
2/1/0.8
0.2/0.3/ND
ND/ND/ND
0.1/2/ND
LEGEND
TCA/DCE/TCE (concentration in ppm)
BOREHOLE
STORM SEWER
CONTAMINANT PLUME (in PPM)
Scale
0
10feet

Figure 5 - Contaminant Delineation with MM-I

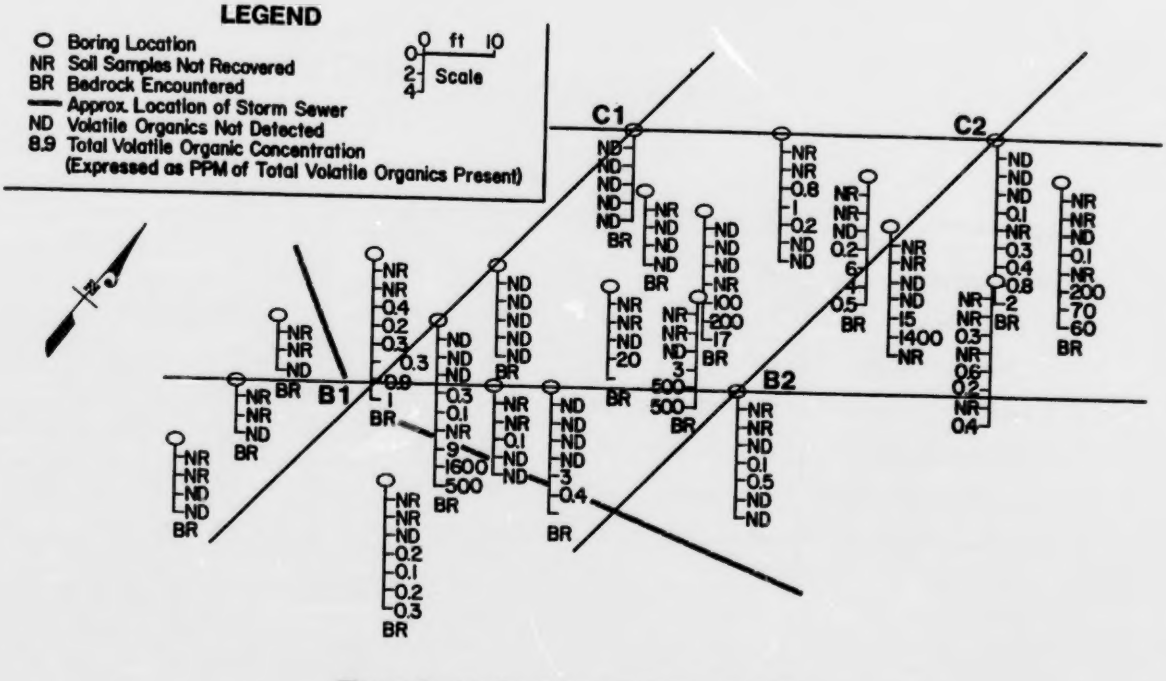
LEGEND
O Boring Location
NR Soil Samples Not Recovered
BR Bedrock Encountered
— Approx. Location of Storm Sewer
ND Volatile Organics Not Detected
8.9 Total Volatile Organic Concentration (Expressed as PPM of Total Volatile Organics Present)
0 ft 10
0
2
4
Scale
C1
C2
B1
B2
NR
ND
BR

Figure 6 - Vertical Contaminant Delineation

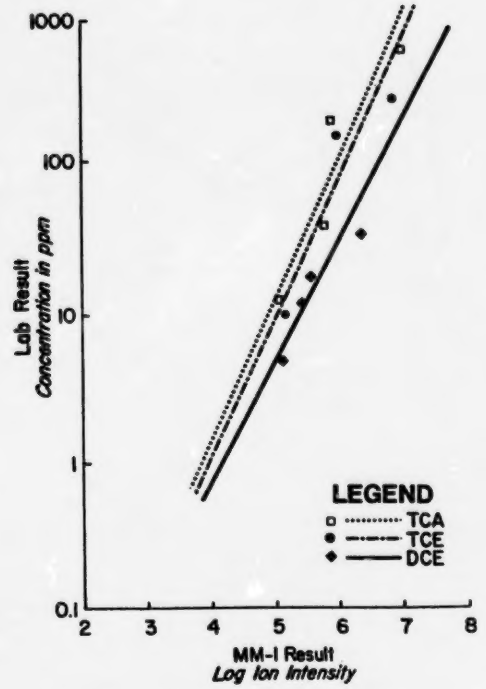

Figure 7 - Comparison of MM-I Ion Intensity to Laboratory Data for Soils

TABLE 1
AGENCY ANALYTICAL RESULTS
(ug/L)

	LOCATION						
	A	B	C	D	E	F	G
chloroform	NF	NF	1.6	3.2	NF	15	NF
chloroethane	NF	20	NF	NF	NF	NF	NF
vinyl chloride	NF	130	3.8	NF	NF	NF	NF
1,1-dichloroethane	NF	100	3.1	NF	NF	NF	NF
1,1-dichloroethene	NF	100	1.1	NF	NF	NF	NF
1,2-dichloroethene	NF	1800	28	NF	5.5	NF	NF
1,1,1-trichloroethane	NF	4600	45	NF	1.8	NF	NF
trichloroethene	NF	750	9.3	NF	5.2	NF	NF

TABLE 2

MM-1 RESULTS FOR MANHOLE WATER SAMPLES (ug/L)

	LOCATION			
	MH 8	MH 10	MH 11	Outlet B
1,1-dichloroethane	NF	NF	NF	NF
dichloroethenes*	NF	NF	NF	NF
1,1,1-trichloroethane	NF	NF	1000	300
trichloroethene	NF	NF	100	50

NF = not found

* includes 1,1-dichloroethene and cis- and trans-1,2-dichloroethene

TABLE 3

MM-1 RESULTS FOR STORM SEWER SAMPLES TAKEN AT CONSECUTIVE JOINTS UPSTREAM OF MANHOLE 11 (ug/L)

	Joint 1	Joint 2	Joint 3	Joint 4	Joints 5 - 7	Joint 8
1,1-dichloroethane	NF	NF	NF	NF	NF	NF
dichloroethenes*	NF	NF	NF	NF	NF	NF
1,1,1-trichloroethane	800	1000	3000	5	5	NF
trichloroethene	100	100	400	NF	NF	NF

NF = not found

* includes 1,1-dichloroethene and cis- and trans-1,2-dichloroethene

TABLE 4

COMPARISON OF LABORATORY RESULTS FOR SOIL SAMPLES IN MG/L TO THE MM-1 RESULTS IN LOG ION INTENSITY

	Sample 1		Sample 2		Sample 3		Sample 4	
	Lab	MM-1	Lab	MM-1	Lab	MM-1	Lab	MM-1
1,1-dichloroethane	0.91	NF	NF	NF	1.1	NF	NF	NF
dichloroethenes*	19.4	5.6	30.3	6.4	4.8	5.1	12.0	5.5
1,1,1-trichloroethane	178	5.9	646	7.1	13.1	5.1	39.0	5.7
trichloroethene	146	5.9	262	6.9	0.6	NF	11.0	5.2

NF = not found

* includes 1,1-dichloreothaene and cis- and trans-1,2-dichloroethene

TABLE 5

COMPARISON OF LABORATORY RESULTS FOR GROUNDWATER SAMPLES IN UG/L TO MM-1 RESULTS IN LOG ION INTENSITY

	Sample 1		Sample 2		Sample 3	
	Lab	MM-1	Lab	MM-1	Lab	MM-1
1,1-dichloroethane	NF	NF	NF	NF	94	NF
dichloroethenes*	NF	NF	58,500	5.9	215	4.2
vinyl chloride	NF	NF	NF	NF	157	NF
1,1,1-trichloroethane	NF	NF	172,000	6.5	29	2.9
trichloroethene	NF	NF	33,000	5.5	122	3.9

NF = not found

* includes 1,1-dichloroethene and cis- and trans-1,2-dichloroethene

TABLE 6
SITE INVESTIGATION COST COMPARISON

	ACTUAL COSTS			ESTIMATED EPA COSTS (*)					
	PEOPLE	DAYS	TOTAL(1)	PEOPLE	DAYS	LABOR(2)	LABORATORY(3)	DRILLING(4)	TOTAL
PHASE I - SITE SCREENING (15 SAMPLES)	2	0.5	$1,350	3	1	$1,200	$12,000	N/A	$13,200
PHASE II - CONTAMINATION LOCATION (43 SAMPLES)	2	1.0	$4,050	4	1.5	$2,400	$34,400	N/A	$36,800
PHASE III - SOURCE DELINEATION (195 SAMPLES)	2	10.0	$47,000	4	15	$24,000	$156,000	$18,000	$198,000
GRAND TOTAL:			$52,400						$248,000

NOTES:
1 - Includes 10 laboratory verification samples based on $800/sample.
2 - Based on $50/hr/person.
3 - Based on $800/sample for method No. 624-625 analysis.
4 - Based on $1200/day/drill rig.
* - US EPA, "Remedial Action Costing Procedures Manual" EPA/600/8-87/049, October 1987.

DETERMINATION OF CHLORDANE IN SOIL BY ENZYME IMMUNOASSAY

Rodney J. Bushway[1], Wayne M. Pask[2], Joan King[1],
Brian Perkins[1] and Bruce S. Ferguson[3]

[1]Professor and Research Associates, Department of Food Science
University of Maine, Orono, ME 04469
[2]Associate Analytical Chemist, Indiana State Chemists Office
Department of Biochemistry, Purdue University, West Lafayette, IN 47907
[3]President, ImmunoSystems, Inc.
Biddeford, ME 04005

ABSTRACT

An enzyme immunoassay (EIA) method has been developed to screen soils for chlordane residues. Soils are extracted with a 10 min sonication in methanol/water (90:10). A 100 ul aliquot is removed from a 1:4 dilution of the sample and added to a polystyrene tube coated with chlordane antibody. Next, 160 ul of chlordane-enzyme conjugate is added to the tube. The chlordane in the sample "competes" with the enzyme-tagged chlordane for the antibody immobilized on the tube. Tubes are incubated at room temperature for 5 min before rinsing with distilled water to remove unreacted sample and enzyme conjugate. Finally, 160 ul each of substrate and chromogen are added and the colored reaction product is allowed to develop for 5 min before the reaction is "stopped" with 2.5N sulfuric acid. Samples can be quantified using a hand-held battery powered photometer which makes possible analysis in the field. Qualitative ("yes-no") results are even simpler to achieve. The linearity range for chlordane is 2.5 to 80 ng/tube. Samples greater than 80 ng can be diluted. Agreement between this method and gas chromatography indicate that the immunoassay procedure would be a good screening test for chlordane residues in soil. Other cyclodienes, including heptachlor, heptachlor epoxide, dieldrin, aldrin, endrin, endrin ketone, chlordene and endosulfan, cross-react making this screening method suitable as a broad spectrum test. EIA's such as this, which are fast, simple, sensitive, and inexpensive are highly suited for rapid, on-site screening of environmental contaminants, particularly at a site where specific residues are suspected.

INTRODUCTION

Chlordane (1,2,4,5,6,7,8,8-octachloro-2,3-3a,4,7,7a-hexa hydro-4,7-methano-1H-indene) an organochlorine insecticide belonging to the cyclodiene group had been used for approximately 40 years against soil and animal pests. However, in 1974 because of its potential health effects (1), the United States Environmental Protection Agency (U.S. EPA) revoked all uses of chlordane except subterranean termite control. Finally, after studies showing that chlordane vapors were present in living areas of treated homes (1-4), the EPA in 1987 cancelled all uses. Even though chlordane is no longer applied, it still poses a substantial environmental threat because of its persistence (5), past widespread distribution (1,6) and potential chronic toxicity (1,4,6). Thus the need to monitor soil around treated houses and toxic waste sites still exists.

Methods presently available to measure chlordane residues in soil are electron capture gas chromatography (7,8) and gas chromatography/mass spectroscopy (6). Both techniques employ very expensive equipment that require experienced technicians. Furthermore analysis is lengthy and cannot be performed in the field. Recently new technology (immunochemical) has been applied to the analysis of pesticides (9). Immunoassay techniques have the advantages of being quicker, less expensive and on site adaptable.

This paper describes an immunoassay for determining chlordane in soil which can be modified slightly for field applications. The method is an excellent screening procedure and shows good agreement with gas chromatographic analyses. Because of the cross reactivity of the chlordane antibody, this immunoassay test has applications for other cyclodiene insecticides.

MATERIALS AND METHODS

Preparation of Pesticide Standards

Chlordane and all other cyclodiene pesticides were obtained from the EPA. Stock solutions of all pesticides were prepared by accurately weighing approximately 10 mg of each into 100 ml volumetric flasks and bringing to volume with methanol. Intermediate standard solutions were obtained by pipetting 0.125 ml endrin, endosulfan and endrin ketone and 0.25 ml of aldrin, dieldrin, chlordane (mixture of alpha 5.9 mg and gamma 4.2 mg/100 ml), heptachlor, heptachlor epoxide and chlordene into 5 ml volumetric flasks and using methanol to bring to volume. Actual working standards were prepared by removing 1, 2.5, 5, 10, 20, 40, 80, and 160 ul aliquots from each of the intermediate standard solutions and adding the aliquots to separate 1 ml volumetric flasks. These standards were brought to volume with 0.75 ml of 0.067M phosphate buffer pH 7.2

containing 0.25% Tween 80 and 25% methanol. Working standards were used to test linearity, cross-reactivity and to make standard curves.

Preparation of Antibody

Chlordane antiserum was prepared by derivatizing chlordane at carbon atom 2 and covalently conjugating it to bovine gamma globulin through a modified carbodiimide crosslinking procedure. Final molar ratio of hapten to globulin was 30:1. Antiserum was prepared in rabbits by multiple sub-cutaneous injections over several months. Blood was collected from the rabbits on a monthly schedule and the serum separated and stored frozen at -10 C.

Preparation of Tubes and Test Kits

Antibodies to chlordane were coated to the walls of polystyrene test tubes by a proprietary method developed by ImmunoSystems. Shelf-life of the dried and stabilized antibody-coated tubes was greater than one year. Horse-radish peroxidase was covalently bound to chlordane ("the Enzyme conjugate") also by a modified carboiimide conjugation technique and is stable in liquid for over 1 year at 4 C. The substrate and chromogen were stabilized buffer preparations of hydrogen peroxide and tetramethylbenzidine (TMB), respectively.

Preparation of Soil

Soil samples for chlordane extraction were first prepared by air drying a sample on Whatman 3MM chromatography paper overnight at room temperature; followed by sieving through a # 10 sieve. The mixed soil was placed in a clean pint mason jar for storage. Sample extraction was performed one of two ways depending upon which analysis was to be used.

Extraction of Chlordane from Soil for Immunoassay

For immunoassay determination 10 g of soil was weighed into a 125 ml Erlenmeyer flask to which 50 ml of (90 + 10) methanol:water was added. This mixture was sonicated for 10 min. A 200 ul aliquot was removed and placed in a 7 ml scintillation vial containing 600 ul of phosphate buffer/Tween 80 solution. Recovery was 90% or better.

Extraction of Chlordane from Soil for GC

Chlordane extraction in soil for gas chromatography (GC) was performed by following the procedure of Saha, 1971 (8). This method could also be used for the immunoassay technique except that a 1 ml aliquot of the acetone:hexane extract must be evaporated to dryness under nitrogen and replaced with 1 ml of methanol.

Analysis of Chlordane by Immunoassay

Soil analysis of chlordane by immunoassay was done by adding 100 ul of the sample from the 7 ml scintillation vial to one of the antibody coated test tubes followed by 160 ul of chlordane "enzyme conjugate". The mixture was allowed to incubate 5 min at room temperature before rinsing (4 times) the unreacted mixture away with water. Substrate (160 ul hydrogen peroxide) was added, followed by 160 ul of chromogen (TMB). After 3 min of incubation the reaction was stopped with 1 drop of 2.5N sulfuric acid. The amount of yellow color was measured by reading the difference in optical density (ΔOD) between the control and each sample at 450 nm with a hand-held battery-powered differential photometer from Artel, Inc. As many as 6 samples plus a control can be run simultaneously without losing accuracy. A control sample (no chlordane present) must be run with each set of tubes since its OD value is used to measure the ΔOD/OD values (where ΔOD is the difference in optical density of the samples or standards from the control divided by the optical density of the control read against water) of the standards and samples.

Analysis of Chlordane by GC

Gas chromatographic conditions were as follows: gas chromatograph, Varian 3700; column, 1/4" x 6', 2 mm I.D. Pyrex glass; liquid phase, 4% SE-30/6% SP-2401; solid phase, 100/120 Supelcoport; oven temperature, 185 C; injector temperature, 270 C; detector temperature, 350; detector type, electron capture (Ni63); carrier gas, nitrogen; flow rate, 30 ml/min; injection volumes, 1-3 ul; integrator, Spectra Physics 4100.

RESULTS AND DISCUSSION

The immunoassay shows a linear relationship (Figure 1) from 25 to 800 ng/ml (2.5 to 80 ng/tube) which was observed between the logarithm of the chlordane concentration and the ΔOD/OD at 450 nm. For samples containing greater than 800 ng/ml a dilution must be made. A ΔOD of 0.88 or greater indicates a sample concentration of more than 800 ng/ml which means the sample should be diluted and the analysis repeated.

Reproducibility results of the chlordane immunoassay can be seen in Tables I and II. Table I shows the consistency data obtained from analyzing standards, different days and over a period of 6 months. Percent coefficients of variation (% CV) range from 17.1 to 5.4, which are excellent for a residue method, but are even greater considering the immunoassay is a screening technique. As one would expect the % CV are lower as the optical density values increase. Although the standards are very reproducible over a long time, it is still recommended for quantification purposes that a 3 point standard curve be performed each day at the 5, 40 and 80 ng chlordane/tube level.

Table II gives results of a reproducibility study on actual chlordane soil samples. Samples range from 0.8 to 897 ppm which is in the normal level of chlordane in soil. It can go as high as 3000 ppm. Like Table I, there was one analysis performed per day, but only for a two week period. The % CV are good with the exception of the 0.8 ppm sample which was 42.9%. However when one considers that all samples are diluted initially 1:4, this makes a sample containing 0.8 ppm near the lower detection limit where higher % CV would be expected. It should be possible to elimate the dilution step on samples less than 1 ppm and thus obtain more consistency. In general the % CV in Table II are slightly higher than the standards (Table I) but both studies indicate that the clordane immunoassay is very reproducible from day to day.

Comparisons were made between the GC and immunoassay methods for chlordane determination in soil (Table III). Seven soil samples were analyzed by both techniques and only for one sample (soil #6) was the agreement between values off by a lot. However, since the immunoassay test would be used as a screening tool all agreements between the seven samples are acceptable. The only criterion that a screening method needs to meet to be successful is to be able to determine the presence or nonpresence of the test compound and be within a certain range of magnitude. Once this is determined then a classical analytical method would be used to determine the exact amount. The chlordane immunoassay meets that criterion.

Perfect correlation between the two chlordane methods is not likely to exist since chlordane is applied as the technical material which contains many different cyclodienes that have different cross-reactivitives. Furthermore, it is possible to have compounds in some soil samples that may interfere nonspecifically with the antibody antigen reactions causing problems.

As mentioned earlier, the immunoassay has cross-reactivity with other cyclodienes (Table IV). The reactivity of the antibody seems to be dependent upon the spatial orientation of the hexa chlorine portion of the cyclodienes since kepone, mirex, gamma chlordene and alpha chlordene do not cross-react while the other dienes do. Of the cyclodienes that cross-react endosulfan, endrin and endrin ketone are the most sensitive. Other noncyclodiene organochlorine pesticides were also tried (like DDT and Lindane) but showed no cross-reactivity.

CONCLUSION

The enzyme immunoassay offers an excellent screening method for chlordane in soil that is reproducible, quick, inexpensive and field adaptable. Furthermore, because of the cross-reactivity of the chlordane antibody, the immunoassay has the potential to be a broad spectrum cyclodiene test. Although only soil was analyzed, it should be possible to modify this assay so that other matrices such as food, air and water could be analyzed for cyclodienes.

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ACKNOWLEDGEMENTS

We thank the Maine Experiment Station for their support. This paper is #1315 of the Maine Agricultural Experiment Station.

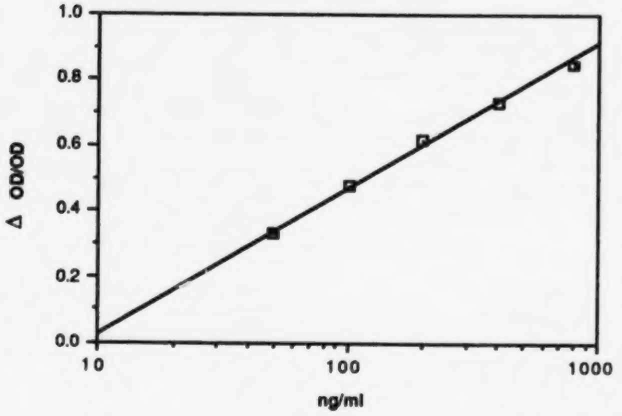

Figure 1- Typical Standard Curve Chlordane in Buffer

Table I- Reproducibility of the Chlordane Immunoassay-Standards in Buffer

	ng/ml				
	50	100	200	400	800
Number of Standard Samples Analyzed	13	47	47	47	47
% Coefficient of Variation	17.1	16.0	13.8	9.9	5.4

Table II- Reproducibility of the Chlordane Immunoassay on Actual Soil Samples Containing Chlordane

	Amount of Chlordane in ppm								
	0.8	3.8	6.9	15.4	81.6	118.3	260.0	630.0	897.0
Number of Samples analyzed	10	7	9	8	8	7	9	8	7
% Coeffient of Variation	42.9	17.3	21.4	18.8	16.7	12.1	11.8	16.9	11.1

Table III- Comparison of the Immunoassay and GC Methods for Determination of Chlordane Residues in Actual Soil Samples

Sample	-ppm Chlordane Found- Immunoassay	GC
Soil-1	37.4	50.0
Soil-2	23.5	20.9
Soil-3	12.1	17.0
Soil-4	23.4	20.9
Soil-5	10.8	16.6
Soil-6	573.0	989.7
Soil-7	1523.0	1600.0

Table IV- Summary of Chlordane Cross-Reactivity Data

Compound	-------ng/ml------- Lower Limit of Detection
Dieldrin	25
Aldrin	25
Heptachlor	25
Heptachlor Epoxide	25
Endrin	10
Endosulfan	10
Endrin Ketone	10
Chlordane	25
Chlordene	15

DEVELOPMENT OF A PROTOCOL FOR THE ASSESSMENT OF GAS CHROMATOGRAPHIC FIELD SCREENING METHODS

M. T. Homsher, V. A. Ecker, M. H. Bartling, L. D. Woods,
and R. A. Olivero, Lockheed Engineering & Sciences Company,
Las Vegas, Nevada 89119

D. W. Bottrell and J. D. Petty,
United States Environmental Protection Agency,
Environmental Monitoring Systems Laboratory-Las Vegas, Nevada 89114

ACKNOWLEDGMENT

We gratefully acknowledge F. C. Garner, M. A. Stapanian, D. Eastwood, P. Wylie, S. Levine, and J. Y. Aoyama for their help on this paper.

ABSTRACT

Advanced field monitoring methods are designed to meet the expanding need for rapid, low-cost field measurements while maintaining data quality that is characterized and adequate to support decision making. The costs and time necessary to acquire environmental data reflect the total of the individual components that include sampling, preparation, analysis, quality assurance, and documentation. The goal of field activities is to minimize or combine functions in order to significantly decrease the time necessary for analytical determination, reporting, and data validation. Specific field techniques that are currently available, such as field gas chromatography, may exhibit data quality characteristics that represent an improvement in information content and integrity over traditional laboratory analytical measurements. The objective of all environmental measurement systems, field and laboratory, is to meet the data quality objectives necessary to support decisions. All analytical systems can be evaluated and compared to identify specific data quality characteristics that determine the applicability and sufficiency for a particular analytical problem based on sensitivity, precision, and accuracy, provided that representativeness, and completeness are equal.

The purposes of this study are to develop a standard procedure for the evaluation of field instrumentation and to apply this procedure to six gas chromatographic systems. In addition, the project will include the investigation of field quality control method components and minimum data documentation. Three-dimensional graphic presentations of the data generated to support this effort have been developed and are demonstrated in this paper. These automated displays allow rapid examination, evaluation, and comparison of data quality characteristics (precision, accuracy, sensitivity, etc.). This procedure is consistent with and supports the USEPA's Data Quality Objective concept that is required for field measurement projects.

BACKGROUND

The Superfund Amendments and Reauthorization Act of 1986 (SARA) is expected to expand the number of National Priority List Sites from the initial 400 to

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1600 [1]. The sampling and analytical capacities of the national analytical laboratories cannot meet this increasing demand for services through the application of currently available Contract Laboratory Program (CLP) resources. In anticipation of this problem, the Analytical Operations Branch (AOB) of the Office of Solid Waste and Emergency Response initiated activities to expand the Program's analytical capabilities. One aspect of these activities involves the investigation of rapid screening methods and field analyses.

Procedures utilizing field portable gas chromatographic instruments are gaining widespread acceptance. Regional and contract personnel routinely use field equipment for rapid, on-site investigations [2]. AOB has established work groups designed to standardize and promote the use of field methods. These groups are involved with evaluating both instrumentation and analytical procedures. The purpose of this document is to describe the activities in progress to assess the status of currently available gas chromatographic field screening instruments and techniques appropriate for the analysis of volatile organics in soil.

INTRODUCTION

In the CLP, soil samples have traditionally been sent from the sampling site to remote laboratories for purge and trap Gas Chromatograph/Mass Spectrometry analysis. In response to the increasing number of sample analyses required, the AOB is currently integrating mobile laboratories and field screening techniques into their analytical repertoire [3].

Field techniques, especially those associated with the analysis of volatile organics, require individual sample/matrix considerations, but utilize common analytical systems. Field analyses have the inherent advantage of providing immediate information relevant to making a specific decision. Results generated from on-site measurements may, however, be subject to a decrease in certainty and defensibility due to variations in Quality Control measures or the use of procedures which have yet to be validated. For many field situations, a rapid response to a problem at a previously characterized environmental site may be more appropriate than investing the increased time and money required to obtain a high degree of certainty in an individual measurement.

As a result of the Regional EPA need to address this situation, the investigation of rapid, field screening methods for volatile organics was initiated. To provide support as quickly as possible, the first phase of the project was restricted to the evaluation of gas chromatographic (GC) systems. This report is likewise restricted to investigative efforts for evaluating field GCs in the analysis of volatile organics.

GUIDANCE FOR FIELD EVALUATION

The objective of this study is the preliminary evaluation of field techniques and field instrumentation. A draft evaluation plan has been outlined that is similar and complementary to parallel projects conducted at the Environmental Monitoring Systems Laboratory-Research Triangle Park (EMSL-RTP) and the Environmental Response Team, Edison, NJ [4], [5]. These studies will provide the information necessary to utilize current instrumentation to generate and document data which are acceptable for specific, defined purposes. The field investigation will identify gaps in current technologies that prevent maximum quality and efficiency of field technologies for on-site field measurements. Manufacturers are active participants in current evaluation efforts. Industry competition will undoubtedly result in the incorporation of instrumental modifications suggested in the course of the field evaluations.

RELATED ACTIVITIES

This study is part of a program which involves multiple related projects, groups, and report requirements. The overall goal is to address many of the problematic sampling and analytical issues associated with the measurement and related confidence interval of volatile analytes. The related studies will be coordinated by a Work Assignment Manager to increase the impact of the individual projects and minimize redundant research efforts.

To date, soil sampling procedures and the effects of alternative preparation techniques have not been extensively investigated. Environmental Monitoring Systems Laboratory-Las Vegas is responsible for the development of a guidance document that will address the areas of sampling techniques and preparation options appropriate for the identification of volatile organics in soil. The resulting document is scheduled for completion in December 1989. Study design issues have been undertaken by the Environmental Research Center of the University of Nevada Las Vegas. Implementation of the study and laboratory support functions will be performed by Lockheed Engineering & Sciences Company (LESC). These activities fit the time frame of the EMSL-LV Field GC Evaluation Study. As a result, soil sampling/preparation options will be evaluated simultaneously with the evaluations of field instrumental techniques and systems. Both sampling and field analytical assessments will be referenced to standard CLP analyses for volatile organics [6]. Considerations basic to this study are the issues of sample storage and preanalytical holding times. These issues have been addressed at Oak Ridge National Laboratory [7]. Local projects will incorporate the findings of this study to maximize long-term relevance and data quality. These studies will provide data for correlation that have not been available previously and will accomplish this with a common reference set of analyses. Each study, if done separately, would require the same degree of reference CLP support. This approach is cost effective, as well as technically valuable.

EXPERIMENTAL DESIGN FOR GAS CHROMATOGRAPHIC FIELD SCREENING METHODS

Replicate analyses of collocated soil samples are a basic concept in the plan to evaluate four field gas chromatographs (GC). Collocated samples are collected so that they are equally representative of a given point in space and time. At each of two sites, soil samples will be taken at 10 to 20 different locations. The homogenized sample from each location will be split into a number of subsamples sufficient to provide three aliquots of soil for each field and laboratory-based instrument. Each of the three subsamples will then be analyzed in triplicate, providing nine replicate analyses per instrument. The data provided by the replicate analyses will be used in the assessment of the field GCs and their evaluation relative to laboratory-based GCs and a gas chromatograph/mass spectrometer (GC/MS). To the extent possible, the same type of chromatography columns will be used in all the instruments. While the ideal experimental design would use completely identical columns, detectors, integrators and operating conditions, this is not possible with the equipment currently available. Table I describes the instrumentation to be utilized in this study.

Prior to mobilization, optimum operating conditions, sensitivity, detector stability and linear range are determined for each field GC. During this bench testing period and on the first day of field activities at each site, five-point calibration curves are created. The ratio of response to concentration (response factor or RF) will be calculated for each target analyte. The Percent Relative Standard Deviation (% RSD) of the RFs from the three middle standard levels must be ≤ 10% for each analyte. The % RSD of the RFs for all five standards must be ≤ 25% for each analyte.

$$RF = \text{mass of analyte/peak area}$$

$$\%\,RSD = \frac{\text{RF Standard Deviation}}{\text{mean RF}} \times 100$$

The calibration curve will be verified each working day by the measurement of three calibration standards at high, medium, and low levels. The RF of each analyte in the continuing calibration standards must be ≤ 25 percent Relative Percent Difference (RPD) with respect to the initial calibration.

$$\%\,RPD = \frac{|RFi - RFc|}{RFi} \times 100$$

RFi = Mean RF from initial calibration

RFc = RF from continuing calibration

In order to provide equivalence, all GC analyses will be performed using the same lots of single component USEPA Quality Assurance Materials Bank (QAMB) Reference Standards. Prior to the initiation of bench and field testing, these standard lots will be analyzed on GC/MS using QAMB standard mixes to demonstrate qualitative and quantitative comparability of the two standard types.

As a means of tracking and documenting the ongoing sensitivity, stability, and precision and accuracy of instrumental measurements, Performance Evaluation Material (PEM) will be prepared using uncontaminated soil native to each of the respective sites. Figure 1 shows the PEM preparation scheme. The compounds to be spiked onto the matrix are dependent upon the particular analytes present at each site. These analytes and their approximate concentrations at each location on the site have been determined in preliminary studies. PEM analyses, at a frequency of one per day and sample location by GC/MS, and three per day and sample location by each GC, will be performed concurrently with each day's sample analyses.

The four field instruments will be evaluated in three different scenarios:

1. Bench testing in the laboratory using standards and performance evaluation material.
2. Field testing using standards, PEM, and soil samples from a local desert site.
3. Comparison testing using standards, PEM and soil samples from a remote, hazardous waste site [8]. Data from this additional site is being included since local desert conditions are not represen-

tative of the majority of hazardous waste sites.

At each phase of the testing, replicate samples and PEM will also be analyzed on the instruments described in Table I.

Comparison of the results of all these analyses establishes the precision, accuracy, and relative sensitivity of the field instrumentation under the described conditions, and the frequency of false positive and false negative rates. Documentation of the analytical conditions will establish guidance for the use of these instruments under field conditions [9].

Figure 2 is a description of a manual headspace [10] technique using an ambient temperature water bath. The use of various aqueous salts to decrease the solubility of analytes in the liquid phase, thus increasing vapor phase concentration may be incorporated into the scheme [11]. A variety of injection techniques [12] may be investigated in an effort to increase the sensitivity of this method while decreasing the variability normally associated with manual headspace injection techniques [13].

Figure 3 is a description of an automated headspace technique using a Hewlett Packard 19395A system coupled to a Varian 3400 gas chromatograph with a photoionization and electron capture detector in series [14]. This type of analysis may represent the future quick-turnaround methods currently under development [15].

Figure 4 is a description of the purge and trap gas chromatograph/mass spectrometer technique modified for the use of a DB-624 0.53mm internal diameter 30 meter column [16], [17]. This reference analysis provides the ability to detect false negatives and false positives [18] which are more probable with the gas chromatograph-only systems, and also provides articulation for comparison with laboratory-based methods.

DATA REPORTING

A series of data reporting forms has been devised to facilitate the accurate, complete and timely reporting of the data [19]. These forms will be field tested during the second and third phases of the assessment. Eventually, the forms may be suitable, after modification during actual use, for the real time transmission [20] of validated analytical results [21], associated quality assurance and quality control data from the laboratory to the field and to appropriate sample control centers.

DATA EVALUATION/DATA QUALITY VECTOR CONCEPT

The purpose of this section of the paper is to demonstrate that quantitative data comparability is possible and may permit rapid, cost effective evaluation of data from several sources at high throughputs while maintaining/improving data quality requirements and identifying data aspects requiring further investigation.

Since each phase of the study (bench and two field locations) will feature analysis of soil samples by three techniques using the same lot of standards, identical performance evaluation samples, and triplicate analyses of collocated samples, sufficient data will be available to effectively compare the three techniques [22]. Review of the literature and the USEPA policies for collecting environmental data center around data quality objectives (DQOs), the precision, accuracy, representativeness, completeness, and comparability (qualitative only) characteristics of the data acquired [23].

In this discussion, the following terms will be used with the understanding that variation in usage from organization to organization does exist. The variability in the definition and use of these terms is a policy issue beyond the scope of this paper.

Accuracy - The degree of agreement of a measured value with the true or expected value of the quantity of concern.

Bias - A systematic error inherent in a method or caused by sample, some artifact or idiosyncrasy of the measurement system or matrix. Temperature effects and extraction inefficiencies are examples of the first kind. Blank contamination, mechanical losses, and calibration errors are examples of the latter kinds. Bias may be both positive or negative, and several kinds can exist concurrently so that net bias is all that can be evaluated, except under special conditions.

To date no official universally accepted detection limit definition has been available nor required by USEPA [24].

Precision - The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions.

Limit of Detection (LOD) - The smallest concentration or amount of some component of interest that can be measured by a single measurement with a stated level of confidence. This is decided by continually diluting a standard solution until no response significantly above noise is noted.

Limit of Quantitation (LOQ) - The lower limit of concentration or amount of substance that must be present before a method is considered to provide quantitative results. By convention, LOQ = 10 So where So is the estimate of the standard deviation at the lowest level of measurement.

Limit of Linearity (LOL) - The upper level of reliable measurement for all practical purposes. Thus, the useful range of the methodology is that range of concentrations between the LOQ and the LOL.

Sensitivity - The ability of the instrument to discriminate between samples having differing concentrations or containing differing amounts of an analyte. This is evaluated by determining the smallest change in concentration which will give a significantly different assay response.

Completeness - A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained.

Representativeness - The degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition.

Comparability - A measure of the confidence with which one data set can be compared to another [25].

As illustrated with the analysis of this data, it is proposed that an estimate of the relative sensitivity of data sets and possibly each sample be used on an analyte-by-analyte basis to provide a measurable data quality vector. The data quality vector will be comprised of an estimate of sensitivity based on the ratio of sample-to-standard area for the same compound, precision expressed as percent relative standard deviation, and percent bias. The frequency of false negative and false positive rates will be examined as well.

Comparison of the three methods used: (1) Manual headspace GC, (2) automated headspace GC, and (3) purge and trap GC/MS will be performed on a compound-by-compound basis in a three-dimensional plot where percent bias is displayed on the x-axis, the ratio of sample area to standard area is displayed on the y-axis, and the percent relative standard deviation (%RSD) is displayed on the z-axis. The influence on the sample-to-standard area ratio will result in an apparent higher concentration standard use than in the absence of an interference from the matrix. On an individual sample basis, the matrix effect could be readily indicated in the three-dimensional plot. The use of this plot will facilitate the rapid visual examination and evaluation of the data against data quality objectives for precision, bias, and the estimate of sensitivity. The location of each point (or a set of points) in this three-dimensional space can be described by the Euclidean distance and direction to a point (or the centroid of a set of points) from the origin or by an appropriate vector notation.

The precision as percent RSD and the accuracy are required attributes of data quality. The ratio of sample-to-standard area provides a quick reference for each sample and analytical method that is unitless but representative of the actual performance of the individual equipment employed in the measurement process. The data quality vector concept can be used to compare various sampling methodologies; an objective of this study as well. The concept of a data quality vector will facilitate the evaluation of sample data against data quality objectives which in turn can reduce the data evaluation and data validation time requirements necessary to support environmental decisions.

Scaling factors may be used to represent an equal or variable contribution for each axis to equitably evaluate the data quality vector for all samples. This scaling is suggested since changes in the precision and accuracy with proximity to the detection limit are expected, as documented in the literature [26].

All quantitation will be performed above the quantitation limit from calibration information for each respective, collocated set of samples for each instrument and method. The use of data only in the region of quantitation [27], may provide an additional feature to increase the timeliness of the data reporting while increasing the information content of the analysis. For the purposes of this study, values below the quantitation limit may be reported as less than the quantitation limit and be excluded from the comparison section of this study. For research purposes, when it is desirable to obtain information near the detection limit, the reporting of estimated values and the area ratio of sample area to the standard area, together with the precision, will be helpful in increasing study information. Conversely, values above the limit of linearity can be reported as greater than values and again be excluded from the comparison, while being scheduled for reanalysis after dilution or resampling, as appropriate. This approach could provide timely information for remediation purposes as well as limiting the field evaluation to only quantitative values. The exception to this approach would be the false negatives and false positive values. A record of false negatives and false positives will be maintained for potential correlation on an analyte-by-analyte and method-by-method basis. The information on false negatives and false positives will be derived from extensive use of known performance evaluation materials and GC/MS analysis. A practical limitation to the assignment of false positives is the greater sensitivity of GC/ECD in comparison to GC/MS. A larger sample may be used for GC/MS analysis to overcome this limitation.

DATA QUALITY VECTOR EXAMPLES

Consider an example when data from the analysis of identical standards using similar analytical techniques occupies the same space, to some known degree of confidence, for precision, bias, and the ratio of sample-standard area. In this situation, the representativeness and completeness are the same for the two analytical techniques since a common lot of standards is in use and completeness is monitored. If these consistent conditions can be provided, then a quantitative comparability statement can be made about the analysis of the same standard by the two analytical techniques.

In practice, this type of approach is used daily in the analysis of environmental samples with the same types of instrument and the same method to provide consistent data of known quality. If this process of comparison of the same standard analyses on different instruments/methods shows promise, then a quantitative comparability statement is possible not only with standards, but also with homogeneous soil performance materials of the same matrix.

The use of the data quality vector plot in these examples based on standard analysis also includes, for illustration purposes, strawman data quality levels, Table 2, based on the past experience of laboratories analyzing thousands of samples [28]. These levels are plotted on Figure 5. In the first example, Figure 5, the detection limit is displayed on the vertical axis; the sample-to-standard ratio replaces detection limit in a later example. The replacement provides a standard ratio unique to each analysis and allows a uniform plot of data from sources with different definitions of detection limit. The percent bias and relative standard deviation axes are labeled. The three data quality levels are displayed as planes for clarity, when in actuality each data quality level is a rectangular solid.

These three-dimensional plots are displayed by an in-house developed computer program written in Pascal language. Interactive manipulation of the display for rotation around any axis or projection onto a plane is possible via keyboard commands or a mouse pointing device. These manipulations provide ready examination of data clusters or data anomalies (outliers).

Data in Table 3 is the basis of a comparison plot, Figure 6, of capillary and packed column volatile GC/MS analysis in a water matrix [29]. Six volatile compounds are listed in Table 3 by percent bias, percent relative standard deviation (%RSD), and detection limit. It would have been preferable to use soil volatile analysis data for this comparison, however, insufficient soil standard analysis data is currently available. The multiple analyte plot of this data in Figure 6 display the capillary column data as squares and the packed column data as triangles. In this plot the general grouping of the data is observed in the vicinity of the data quality level I in Figure 6. Closer inspection of Table 3 and Figure 6, however, reveal that in several instances, this data does not meet the percent bias and percent RSD criteria for data quality level I, and actually is data quality level II for these two attributes. In addition, disparity between percent bias and percent RSD for specific analytes in the two types of analysis becomes more apparent in Figure 7. In this figure, a projection along the detection limit axis plots only percent bias and percent RSD. The individual points have been labeled sequentially according to their order in Table 3 for comparison purposes. The capillary column data is again depicted with a square shape, while the packed column data is depicted by a triangular shape. For this data, generally the capillary column data displays a lower % RSD since it is single laboratory data. The most startling disparity is the difference between the percent bias for compound number 2 (1,2-dichloroethane). The capillary column value (-30%) almost exceeds the data quality level II criteria for percent bias. A reversal of bias is also seen for compound 3 (trichloroethene). In both instances, this observed difference is statistically significant at the one percent (1%) significance level. Since the single laboratory data only consists of six points, insufficient data is present for conclusion without further verification. The three-dimensional plot does bring out the direction and magnitude of the differences in a graphic fashion for further investigation.

In the second example, data from Table 4, the results of repetitive GC standard analysis by purge and trap and static headspace analysis at a 20 microgram per liter concentration is displayed in a three-dimensional plot for a single analyte tetrachloroethene in Figure 8. The sample-to-standard data has been modeled from ratios reported by Wylie, et al. in this comparison, and area ratio replaces the detection limit axis seen in the first example. Both the percent bias and percent RSD axes are labeled in Figure 8. The purge and trap data is depicted as a triangle and the headspace data is depicted as a square.

The printed page shown as Figure 8 lacks the perspective and versatility of the computer monitor; however, two distinct clusters are observed with approximately equal percent bias range. The discriminating feature in the display is the lower percent RSD for the headspace analysis.

This distinction is more apparent in Figure 9, a two-dimensional projection of Figure 8. The ability to achieve comparable area ratio and percent bias, with superior (lower percent RSD) precision by headspace analysis was possible by using a larger sample volume in the headspace vial, an elevated equilibrium temperature, addition of a salt solution to the standard, and use of equal equilibration times for each headspace vial.

In the third example, the preliminary field data in Table 5 from the analysis of the same volatile soil performance evaluation material by five field gas chromatographics and one laboratory gas chromatograph is considered. The three-dimensional plot in Figure 10 displays percent RSD, percent bias, and sensitivity. A two-dimensional projection of the data in Figure 11 on the precision and bias axes, together with the Strawman data quality values, displays the relative performance of these systems for a single analyte in soil.

The three-dimensional plot of this data can be rotated in space by the computer program for different perspectives as well as be examined by statistical techniques [30], principal component analysis, pattern recognition techniques [31], and projected onto two axes for easier two-dimensional comparisons.

With the inclusion of the overlay of the strawman data quality objectives (Figure 10), an individual compound or element data point or a series of data points may be examined for possible relationships simultaneously. The use of this plot for sampling and analysis data display, together with the data quality vector concept, represents an opportunity to bring quantitative comparability and powerful data analysis techniques to provide data of known quality to the data user in a more timely and useful format.

CONCLUSIONS

Recent reported advances in the literature such as 30-second [32], and 5-second GC analysis [33], and the use of automated and robotic systems for volatile analysis will require advances in data reporting, validation, comparison and interpretation. The use of procedures such as this for rapid, accurate data validation and interpretation may optimize the information content of analytical results and decrease the time required to supply validated environmental data to the data users. The procedures described here have been applied to the evaluations of currently available field instrumentation, sample preparative options, and analytical techniques. This work collectively supports the development of an integrated approach to directly present field screening alternatives in the context of data quality objectives.

NOTICE

Although research described in this article has been funded wholly by the United States Environmental Protection Agency under contract number 68-03-3249 to Lockheed Engineering & Sciences Company, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute Agency endorsement of the product.

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PERFORMANCE EVALUATION MATERIAL PREPARATION SCHEME

Performance Evaluation Materials (PEMs) being used in the study are site-specific. Each matrix is native to the sampling site, and each spiking solution contains analytes determined, through CLP analyses, to be present at the site.

MATRIX PREPARATION

- Soil Source Determination

  Uncontaminated location on sampling site
  Physical characteristics similar to contaminated soil

- Soil Homogenation

- Soil Aliquotting According to Analytical Method

INST/METHOD	SAMPLE CONTAINER	SAMPLE WT.
GC/Manual Headspace	40 mL VOA Vial	12 g
GC/Automated HS	20 mL Crimp-top Vial	10 g
GC/MS	40 mL VOA Vial	5 g

MATRIX SPIKING

- Spiking Levels 25 ng/g and 125 ng/g
  Analyte concentrations chosen to be above the practical quantitation limit and within the linear range of all instrumentation.

- Spiking Compounds
  Site-specific spiking solutions include various combinations of the following analytes:

  Benzene
  Toluene
  Ethylbenzene
  P&M-Xylenes (co-elute)
  O-Xylene
  Chloroform
  Chlorobenzene
  Trans-1,2-Dichloroethylene
  1,1,1-Trichloroethane
  Trichloroethylene
  Tetrachloroethylene
  1,1,2,2-Tetrachloroethane

PEM STORAGE AND SHIPMENT

Immediately after spiking, each container is tightly capped and replaced in the original shipping boxes. To reduce analyte loss and/or contamination during shipment, the boxes are:

- Heatsealed in Scotchpak bags
- Stored at 4 degrees C until shipment
- Shipped and stored on site in clean ice chests containing freeze gel packs

FIGURE 1

SAMPLE PREPARATION (Triplicate Subsamples for Each Instrument)

Sample Size: 12 g 0.5 g

Sample Container: 40 mL screw-top VOA vial with PTFE septum

Surrogate/RT Standard Addition: 10 mL of carbon-free water containing a non-target compound RT standard at a concentration equivalent to 50 ug/Kg is injected through septum. (One of several possible aqueous salt solutions may be substituted for chlorine-free water.)

Sample Equilibration: Sample vial is shaken for 15 seconds, placed in a water bath at ambient temperature for 15 minutes and shaken for 15 seconds prior to each injection.

SAMPLE ANALYSIS

Sample Injection: 500 uL of sample headspace is withdrawn through the septum with a gas-tight syringe and injected into the GC.

Instrument Parameters: Varian 3400, Column - J&W 30 m x .53 mm DB-624
FSCC. Carrier gas flow - He at 8 mL/min
Make-up gas flow - N2 at 40 mL/min
Injector Temperature: 130 degrees C
HNU Model PI-5202 PID
PID Temperature: 200 degrees C
PID Lamp Intensity: 45% full scale
ECD Temperature: 200 degrees C

GC Temperature Program: Initial Temp. - 60 degrees C
Initial Time - 5 min.
Program Rate - 10 degrees C/min
Final Temp. - 130 degrees C
Final Time - 3 min.

Parameters for Field GCs will be determined during bench testing.

DATA REDUCTION

Integrators: Hewlett-Packard 3396A

Data Processing: Zenith Portable Computer Model ZFL-181-93 formatted with Lotus Spreadsheet.

FIGURE 2

MANUAL HEADSPACE SAMPLE ANALYTICAL SEQUENCE

SAMPLE PREPARATION (Triplicate Subsamples for Each Instrument)

Sample Size: 10 g 0.5 g

Sample Container: 22 mL headspace vial, PTFE-faced silicone rubber septum, aluminum crimp cap

Surrogate/RT Standard Addition: 10 mL of chlorine-free water containing an RT standard at a concentration equivalent to 50 ug/Kg is injected through the septum. (One of several possible aqueous salt solutions may be substituted for chlorine-free water.)

Sample Equilibration: Samples are equilibrated for 30 minutes in a 60 degree C heated carousel prior to analysis.

AMPLE ANALYSIS

HP 19395A Headspace Sampler Settings: Sampler Bath Temp. - 60 degrees C
Sample Loop Size - 1 mL
Sample Loop Temp. - 100 degrees C
Carrier Gas HE at 6 psi
Auxiliary Pressure 1 psi

Headspace Injection Sequence and Set Point Display: Probe Down 01
Start Pressurization 03
Stop Pressurization 13
Start Venting 14
Stop Venting 25
Start Injecting 26
Stop Injecting 227
Probe Up 228

Instrument Parameters: As for manual headspace analysis using Varian 3400 GC and J&W DB-624 column 30 m x .53 mm

GC Temperature Program: As for manual headspace analysis

DATA REDUCTION

As for manual headspace data reduction.

FIGURE 3

AUTOMATED, HEATED HEADSPACE SAMPLE ANALYTICAL SEQUENCE

SAMPLE PREPARATION

Sample Size: 5 g 0.1 g A smaller sample weight may be used if screening analyses indicate a high level of volatile contamination.

Sample Container: 40 mL screw-top VOA vial with PTFE septum. The final sample aliquot is weighed into a purge device.

Surrogate/Internal Standard Addition: 5 mL of reagent water containing Internal Standards and Surrogate Standard as indicated in the EPA protocol [17] is added to the purge device.

SAMPLE ANALYSIS

Purge and Trap Conditions: Trap Configuration - 1 cm. Supelco 3% SP-2100 on 60/80 chromosorb, 15 cm Tenax, 8 cm 35/60 silica gel

Purge Flow Rate - 30 mL/min.
Purge Time - 11 min.
Desorb Temperature - 200 degrees C (4 min.)

Instrument Parameters: Finnigan 4021-D GC/MS
J&W DB-624 FSCC 30 m x .53 mm
Carrier Gas - He at 15 mL/min.
Makeup Gas - He at 40 mL/min.
Separator Oven Temperature - 260 degrees C
Injector Temperature - 260 degrees C
Ionizer Temperature - 250 degrees C
Scan Time: 2 sec/scan

GC Temperature Program: Initial Temperature - 10 degrees C
Initial Time - 3 min.
Program Rate #1 - 10 to 40 degrees at 5 degrees C/min.
Program Rate #2 - 40 to 140 degrees at 10 degrees C/min.
Final Temperature- 140 degrees C

DATA REDUCTION

Data System: Finnigan INCOS Model 2400

FIGURE 4

GC/MS SAMPLE ANALYTICAL SEQUENCE

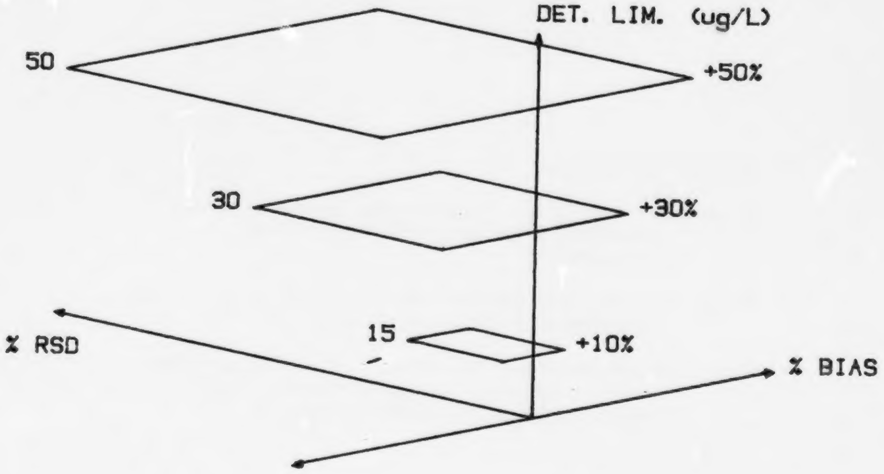
DET. LIM. (ug/L)
50
+50%
30
+30%
15
+10%
% RSD
% BIAS

FIGURE 5

STRAWMAN VOA DQO'S

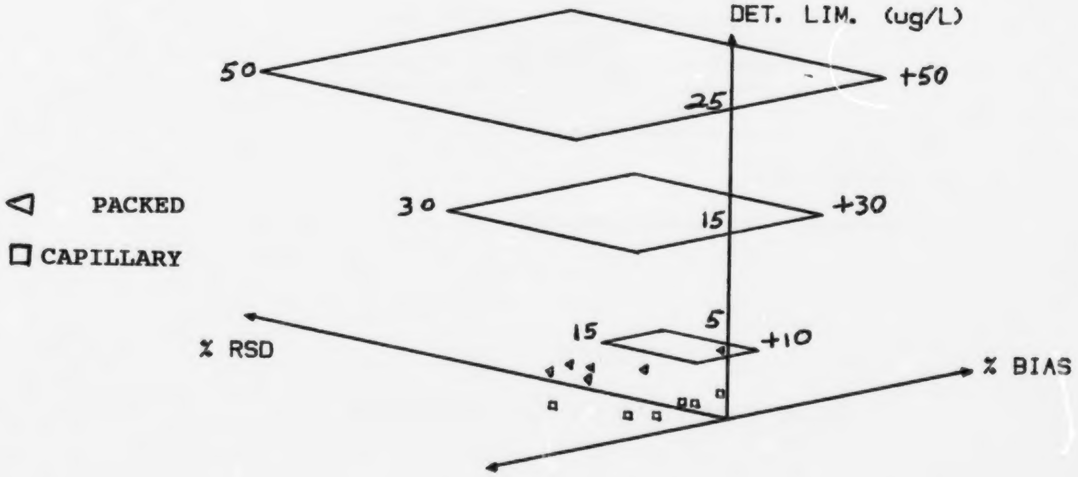

FIGURE 6

DATA COMPARABILITY PLOT EXAMPLE
VOA CAPILLARY AND VOA PACKED COLUMN ANALYSES

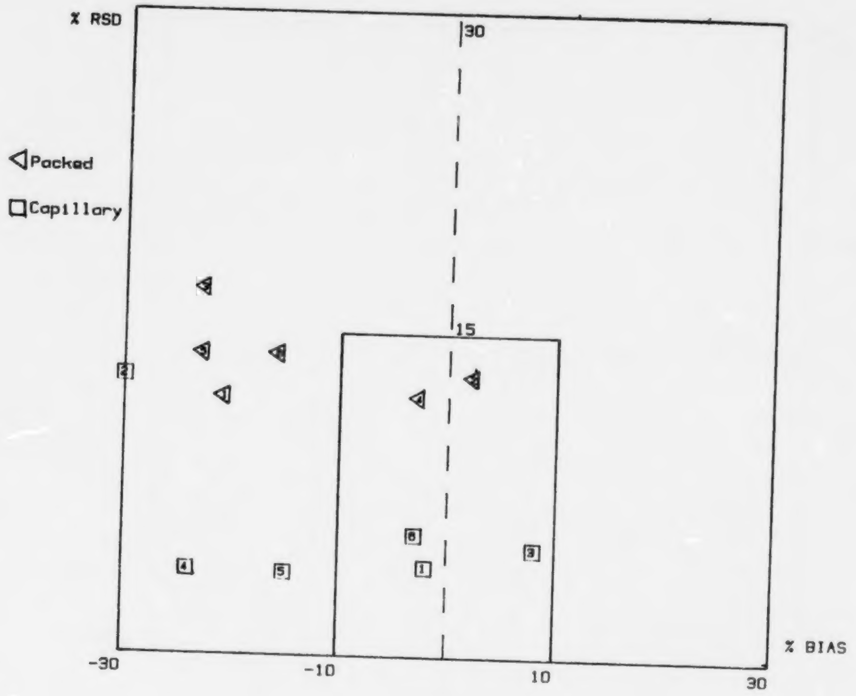

FIGURE 7

TWO-DIMENSIONAL DATA QUALITY PLOT (Multiple VOA Analytes)

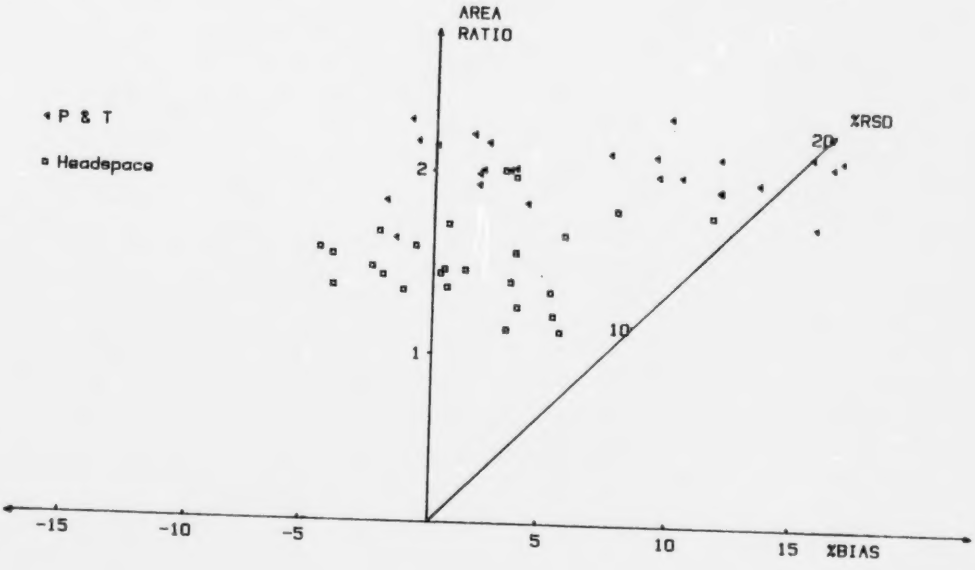

FIGURE 8

COMPARISON THREE-D PLOT OF PURGE & TRAP AND HEADSPACE QC DATA

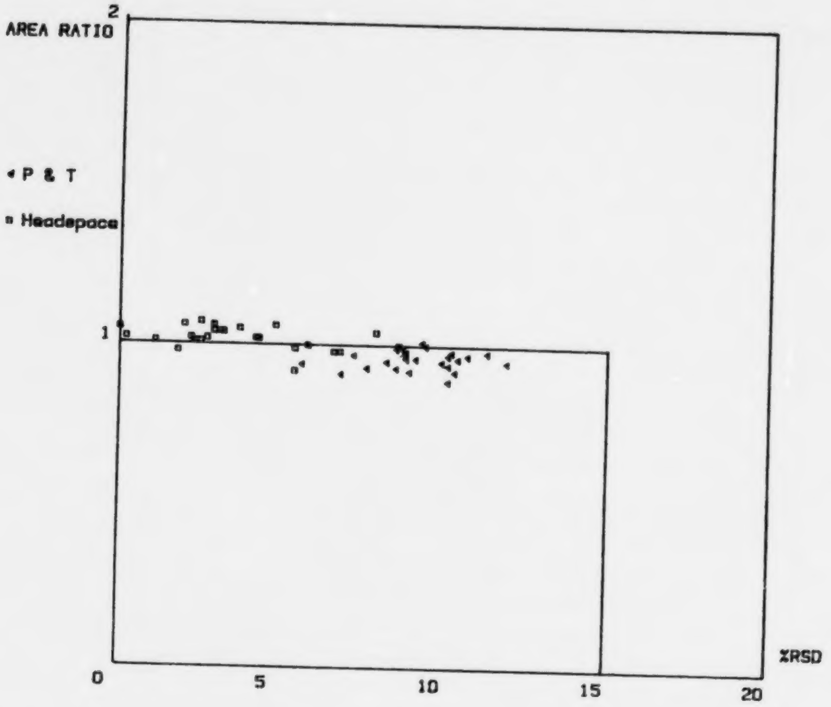

FIGURE 9

TWO-DIMENSIONAL DATA QUALITY PLOT P & T VS. HEADSPACE GC

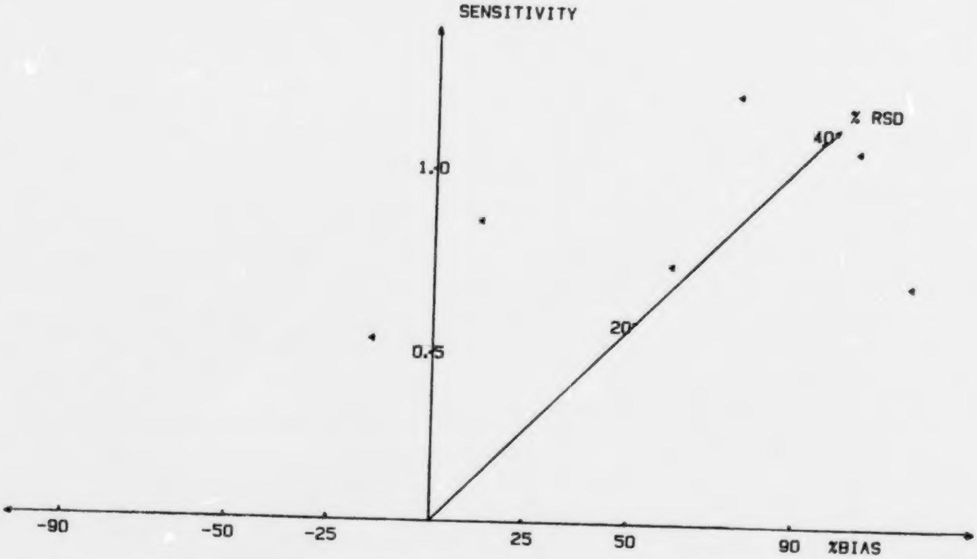

FIGURE 10

3-DIMENSIONAL PLOT OF INSTRUMENT COMPARISON DATA

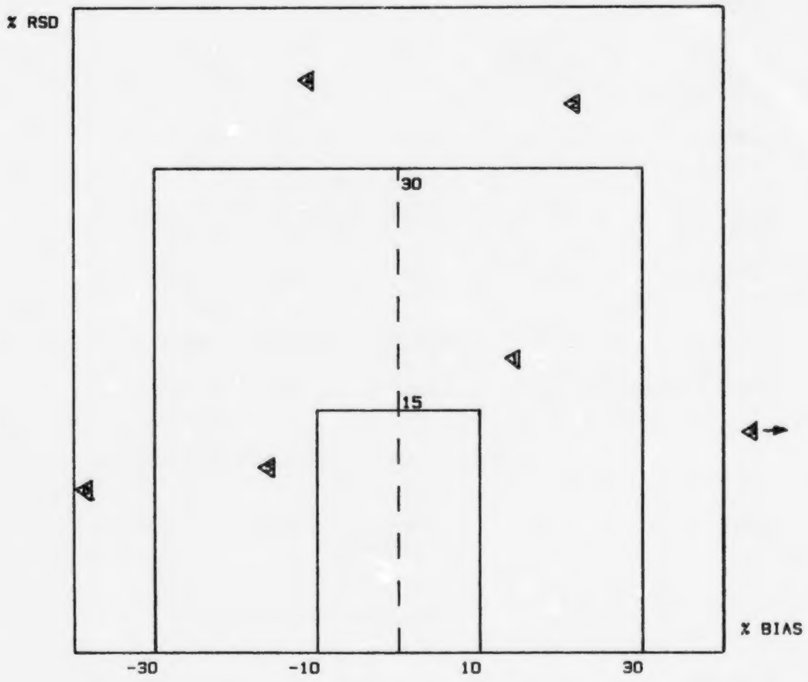

FIGURE 11

TWO-DIMENSIONAL DATA QUALITY PLOT - MULTIPLE INSTRUMENT COMPARISON

TABLE I

INSTRUMENT CONFIGURATIONS

MANUFACTURER	MODEL NO.	DETECTOR(S)	TEMP PROG	INJECT TYPE	COLUMN TYPE
FIELD GAS CHROMATOGRAPHS					
HNU SYSTEMS INC.	321	ECD	NO	SPLIT-LESS	CAP
SHIMADZU SCIENTIFIC INSTRUMENTS	MINI-2E	ECD	NO	SPLIT-LESS	CAP
PHOTOVAC INTERNATIONAL	10S50	PID	NO	SPLIT-LESS	*CAP
SCIENTIFIC REPAIR INC.	8610	ECD	NO	SPLIT-LESS	CAP
THERMO ENV.	AID 511	PID	NO	SPLIT-LESS	PACKED
MOBILE LAB GAS CHROMATOGRAPH					
HEWLETT-PACKARD	5880	PID,ECD	YES	SPLIT-LESS	CAP
FIXED LABORATORY GAS CHROMATOGRAPH					
VARIAN	3400	PID,ECD (IN SERIES)	YES		CAP
FIXED LABORATORY GC/MS					
FINNIGAN	4021D	MASS SPEC	YES	PURGE & TRAP	CAP

GC INTEGRATORS

HEWLETT-PACKARD 3396A

ANALYTICAL COLUMNS

MANUFACTURER	TYPE	LENGTH	I.D.	FILM THICKNESS
J&W SCIENTIFIC	DB-624	30m	0.53mm	3.0 micron
*PHOTOVAC	CPSIL-5	10m	0.53mm	2.0 micron

TABLE II

3-LEVEL DATA QUALITY STRAW MAN-VOA

LEVEL I	LEVEL II	LEVEL III
RSD $\leq$ 15%	15 < RSD $\leq$ 30%	30 < RSD $\leq$ 50%
$\lvert$BIAS$\rvert \leq$ 10%	10 < $\lvert$BIAS$\rvert \leq$ 30%	30 < $\lvert$BIAS$\rvert \leq$ 50%
DL $\leq$ CRQL	CRQL < DL $\leq$ 3*CRQL	3 CRQL < DL $\leq$ 5*CRQL

CRQL - CONTRACT REQUIRED QUANTITATION LIMIT
% RSD = 100 x S.D./$\bar{X}$
% BIAS = 100 x ($\bar{X}$ - T)/T
T - TRUE OR REFERENCE VALUE
$\bar{X}$ - MEAN OF THE MEASURED VALUE

TABLE III

COMPARISON DATA FOR PACKED AND CAPILLARY COLUMN VOA STANDARD GC/MS ANALYSIS

	% BIAS		% RSD		DET. LIMIT ug/1	
	PACKED	CAP	PACKED	CAP	PACKED	CAP
1. Chloroform	-21	-2	12	4.2	2.9	0.90
2. 1,2-Dichloroethane	2.4	-30	13	13	2.8	1.2
3. Trichloroethene	-23	8	17	5.1	3.1	1.1
4. Benzene	-3	-24	12	4	2.7	1.1
5. Toluene	-23	-15	14	3.9	3.9	0.64
6. Chlorobenzene	-16	-3	14	5.7	3.3	0.91

TABLE IV

COMPARISON DATA STANDARD GC ANALYSIS BY PURGE AND TRAP VERSUS HEADSPACE TECHNIQUES

	N	% Bias	Precision % RSD	Estimate of Sensitivity Sample area/Standard area
Purge and Trap	25	-1	9.2	.96
Headspace	25	-1.4	3.7	1.01

TABLE V

PRELIMINARY FIELD DATA

GC/ECD 1,1,2,2-TCA RESULTS FROM
THE ANALYSIS OF PERFORMANCE EVALUATION MATERIALS

INSTRU. I.D.	INJ. VOL.	SENSITIVITY	% BIAS	% RSD
1	100 ul	.221	+14.0	18.1
2	25 ul	.119	+21.3	33.9
3	100 ul	.295	+83.2	13.6
4	25 ul	.227	-11.4	35.4
5	100 ul	.513	-16.3	11.4
6	500 ul	.226	-38.8	10.0

LESC CONTRIBUTORS

E. Neil Amick
Marilew H. Bartling
Kevin A. Cappo
John W. Curtis
Betty A. Deason
Vicki A. Ecker
Forest C. Garner
Clare L. Gerlach
Michael T. Homsher
Henry B. Kerfoot
Tim E. Lewis
William D. Munslow
Ramon A. Olivero
Eric A. Steindl
Larry D. Woods
John H. Zimmerman

COST ANALYSIS FOR USING MOBILE LABORATORIES VERSUS FIXED-BASE LABORATORIES FOR SITE CHARACTERIZATION AT FUSRAP SITES

Gomes Ganapathi, Ph.D. and David G. Adler
Bechtel National, Inc.
800 Oak Ridge Turnpike
Oak Ridge, Tennessee 37830

Mark Carkhuff
Weston Analytical Laboratory
208 Welsh Pool Road
Lionville, Pennsylvania 19353

ABSTRACT

This report outlines the potential cost savings from using mobile analytical laboratories as compared to fixed-base laboratories. The costs of using a mobile laboratory for characterizing sites for chemical contaminants are compared to the costs of employing fixed-base laboratories. Cost estimates were based on discussions with commercial analytical laboratories, Bechtel National, Inc. experience with site characterization activities, and analyses conducted in-house. Results from the comparative analysis for three hazardous waste sites are presented.

Unlike fixed-base laboratory analyses, costs for mobile laboratory work are generally not calculated on a cost-per-sample basis. Rather, costs are determined by the number of days the laboratory is rented for on-site use. Although site characterization using on-site mobile laboratories is generally less expensive, this cost advantage can easily be lost due to poor planning or unexpected delays in sampling activity while the laboratory is on site. Strategies for coordinating sampling and analysis activities that minimize the time frame for employing a mobile laboratory are presented.

1.0 INTRODUCTION

Bechtel National, Inc. (BNI) is conducting Remedial Investigation/ Feasibility Studies (RI/FS) as part of the Department of Energy's (DOE) Formerly Utilized Sites Remedial Action Program (FUSRAP). FUSRAP is a program managed by DOE to identify and clean up or otherwise control sites where residual radioactive contamination (exceeding current guidelines) remains from activities carried out under contract to the Manhattan Engineer District and the Atomic Energy Commission during the early years of the nation's atomic energy program, or from commercial operations causing conditions that Congress has mandated DOE to remedy.

This report outlines the potential cost savings from using mobile analytical laboratories for site chemical characterization. The costs of using a mobile laboratory for characterizing sites for chemical contaminants are compared to the cost of employing a fixed-base laboratory. Cost estimates are based on BNI experience with site characterization activities, discussions with commercial analytical laboratories, and analyses conducted in-house. Results from the comparative analysis for three FUSRAP sites are presented.

2.0 OVERVIEW OF SAMPLING AND ANALYSIS STRATEGIES FOR FUSRAP SITES

As with all waste site characterization strategies, the objectives of sampling and analysis tasks for the FUSRAP sites are

- to determine the nature and extent of contamination (radiological characterization being the major effort)
- to quantitatively and qualitatively characterize the contamination in all media of concern
- to identify contaminant transport pathways
- to assist in the planning of site remedial actions

2.1 Contract Laboratory Program and Mobile Laboratory Use

Compliance with Contract Laboratory Program (CLP) requirements by fixed-base laboratories ensures that all analytical data generated are subject to rigorous

Quality Assurance/Quality Control (QA/QC) protocols and extensive evidential documentation. As such, data generated using these protocols are "litigation quality" data. The acceptability of mobile laboratory data and results from other relatively new field analysis techniques have not been tested in courts.

Recent drafts of the Environmental Protection Agency (EPA) RI/FS guidance document (Ref. 1) and Data Quality Objectives document (Ref. 2) recommend that tasks such as risk assessment, Potentially Responsible Parties determination, and remediation validation activity be supported by CLP analytical results. An increasingly common practice is to rely on field techniques for most of these activities and screening, and then to use fixed-base laboratories to confirm field results. EPA generally promotes these techniques as a means of saving time and money during site characterization activities (Refs. 2 and 3).

The methods expected to be applicable to FUSRAP site characterization activities include the use of mobile laboratories fitted with gas chromatograph-flame ionization detectors (GC-FID) for on-site soil-gas/liquid organics analysis, and atomic absorption (AA) techniques for inorganics analysis. It is, however, important to recognize that field analytical techniques will never replace the role of fixed-base laboratories.

3.0 COST ANALYSIS

This section provides estimates of the relative cost-effectiveness of employing a mobile laboratory versus a fixed-base analytical laboratory for site characterization purposes. The analysis used site characterization plans for the FUSRAP Colonie site in New York, the St. Louis Airport Site (SLAPS) in Missouri, and the Tonawanda site in New York as a basis for cost comparisons.

Cost estimates were calculated for two separate characterization options. Under Option A, sites were characterized using an on-site mobile laboratory. Option A costs include the cost of sending 10 percent of all samples (as duplicates) to a fixed-base CLP laboratory for confirmation. Under Option B, all samples are analyzed by a fixed-base CLP laboratory.

For each site, three Option A costs are provided. These three estimates reflect the costs that would accrue for three different time periods (7 days, 14 days, and 30 days) that the mobile laboratories would be on site. The results from the comparative cost analysis are provided in Table I.

Table I
MOBILE LABORATORIES VERSUS FIXED-BASE LABORATORIES: A COST COMPARISON FOR SLAPS AND THE COLONIE SITE

SITE / SAMPLES	ST. LOUIS AIRPORT SITE			COLONIE SITE		
Groundwater Samples	51			24		
Surface Water Samples	4			5		
Soil/Sediment Samples	46			126		
TOTAL SAMPLES	101			155		
TURNAROUND TIME / OPTION	7 days	14 days	30 days	7 days	14 days	30 days
A. Mobile Lab plus confirmation at CLP Lab (10%)	$57,100	$76,000	$107,000	$28,800	$44,700	$51,700
B. Fixed-Base, CLP Lab	NA	NA	$102,000	NA	NA	$67,200
SAVINGS DUE TO OPTION A VERSUS OPTION B	$44,900 44%	$26,000 25%	(-$5,000) (-5%)	$38,400 57%	$22,500 33%	$15,500 23%

Table Notes:

1. All samples analyzed for volatiles, semivolatiles, metals, and indicator ions as required by field sampling plans.
2. Identical instrumentation (GC/FID and AA) used by both the mobile and fixed-base laboratories.
3. Costs for the mobile laboratory include transportation, technician per diem, and all required reagents and other support items.
4. Fixed-base laboratory costs include an assumed packaging and shipping cost of $50/sample.

After discussing these results with appropriate FUSRAP personnel, it was determined that significant cost savings are possible through the use of mobile laboratories. However, cost savings are tied to the length of time the mobile laboratory must be on site. This is generally determined by the rate at which samples can be generated, not the rate at which samples can be analyzed by the mobile laboratory.

3.1 SLAPS, Missouri

Borehole sampling at the SLAPS took almost 60 days, due to difficulties in mobilizing drilling rigs. This was substantially longer than anticipated. If a mobile laboratory had been employed for this site, it would have been under utilized and the costs of site characterization would have been much higher than if a fixed-base laboratory were employed.

The number of days that BNI rents a mobile laboratory could be reduced by beginning drilling operations a few days before the mobile laboratory arrives on site. However, the benefits of this phased approach would be limited by the allowable holding time for volatile organics samples (7 days).

3.2 Colonie Site, New York

Figure 1 provides a proposed phased schedule for sampling and analysis at the Colonie site using a mobile laboratory. With this schedule, the mobile laboratory is never "overloaded" with samples, the sample generation rate is reasonably achievable, and no samples would be held in excess of allowable holding times. Using this approach and schedule, a savings of approximately 33 percent should be possible for chemical analysis, even assuming that 10 percent of all samples are duplicated for analysis in a fixed-base laboratory.

ACTIVITY	COLLECT SAMPLES	DAY	ANALYZE SAMPLES
	5 SW+5 SD SAMPLES	1	
	11 GW SAMPLES	2	
MOBILIZE DRILL-RIG	12 SL SAMPLES	3	
	12 SL SAMPLES	4	
MOBILIZE MOBILE LAB	12 SL SAMPLES	5	5 SW+5 SD SAMPLES
	12 SL SAMPLES	6	11 GW SAMPLES
	12 SL SAMPLES	7	11 SL SAMPLES
	12 SL SAMPLES	8	11 SL SAMPLES
	12 SL SAMPLES	9	11 SL SAMPLES
	12 SL SAMPLES	10	11 SL SAMPLES
	12 SL SAMPLES	11	11 SL SAMPLES
	13 SL SAMPLES	12	11 SL SAMPLES
	13 NEW GW SAMPLES	13	11 SL SAMPLES
DEMOBILIZE DRILL-RIG		14	11 SL SAMPLES
		15	11 SL SAMPLES
		16	11 SL SAMPLES
		17	11 SL SAMPLES
DEMOBILIZE MOBILE LAB		18	13 NEW GW SAMPLES

(TOTAL = 155 SAMPLES ANALYZED IN 14 DAYS)

NOTE:

GW - GROUNDWATER
SD - SEDIMENT
SL - SOIL
SW - SURFACE WATER

FIGURE 1
PROPOSED SAMPLING AND ANALYSIS SCHEDULE
USING A MOBILE LABORATORY
FOR COLONIE FUSRAP SITE

3.3 Tonawanda Site, New York

A third cost comparison between the use of mobile laboratories versus fixed-base laboratories for site characterization was analyzed for the Tonawanda site in New York. Although radiological and chemical contamination was suspected at the site, no information on the location or magnitude of contamination was available to guide placement of the monitoring wells.

Project geologists were presented with the site background and asked to estimate the number and type of sampling locations that would be necessary to adequately characterize the site. The geologists predicted that the number of soil borings required under both options would be identical, since radiological characterization would not be assisted by the mobile chemical analysis laboratory. However, the availability of quick turnaround, on-site chemical analysis was predicted to reduce the number of groundwater monitoring wells required by 10 percent.

The relative costs of these two approaches are shown in Table II. As with the Colonie and SLAPS analyses, significant potential cost savings are apparent. The magnitude of the savings is explained primarily by the cost savings associated with analyzing a very large number of samples (a total of 120) on site.

TABLE II
CHEMICAL SAMPLING AND ANALYSIS COST BREAKDOWN DETAILS FOR OPTIONS A AND B
FOR TONAWANDA, NEW YORK SITE

Task Details	OPTION A		OPTION B	
	Quantity	Mobile Lab +10% CLP Costs For 20 Days	Quantity	Fixed-Base Lab Costs
Soil Gas - Sampling, Analyzing	30 Samples	$ 6,100	30 Samples	N/A
Soil Boring, Sampling, Packing, Shipping	15 LF/30 Samples	$ 45,100	15 LF/30 Samples	$ 45,900
Surface Water + Sediment Sampling, Packing, Shipping	20 SW + 20 SD	$ 2,700	20 SW + 20 SD	$ 3,600
Per diem, Travel, Stay, Etc.		$ 3,000		$ 2,200
Analysis Samples	100		100	
QC Samples	20		20	
Metals	AA		AA	
VOCs	GC/FID		GC/MS	
BNAEs	GC/FID		GC/MS	
IONs	YES		YES	
Analytical Cost		$ 36,400		$ 121,500
TOTAL		$ 93,300		$ 173,200
SAVINGS USING MOBILE LAB		$ 80,000		

A summary of typical analytical levels and qualitative differences between a fixed-base laboratory and a mobile laboratory is presented in Table III. This summary is in reference to analysis only.

4.0 CONCLUSION

When properly equipped, mobile laboratories can offer essentially the same list of services provided by fixed-base laboratories. On-site

TABLE III
FIXED-BASE LABORATORY VERSUS MOBILE LABORATORY - A SUMMARY OF QUALITATIVE DIFFERENCES

Factors	Fixed-Base Lab Equipped With All CLP Instruments (GC/MS/AA/ICP)	Field Deployable Analytical Instruments		
		GC/FID	GC/MS	AA/XRF
Type of Analysis	Hazardous Substance List (HSL) organics/inorganics	Volatiles and a few semivolatiles	HSL organics	HSL inorganics
Resolution (ppm/ppb)	Very high (ppb)	High/need MS for finer resolution (low ppm to high ppb)	Very high (ppb)	AA - Very high (ppb) XRF - Medium (ppm)
Data Quality	- Stringent QA/QC - Standard Methods	Dependent on QA/QC steps employed/required		
Qualitative/Quantitative Results	Quantitative	Quantitative	Quantitative	Quantitative
Cost of Equipment (in a scale of 0 to 10)	10 (including support facilities)	6	8	7
Cost of Analysis (per sample cost)	$1,000/Sample (Organics) $200/Sample (Metals) (because of strict QA/QC)	$100/Sample or $1,500-$2,000/day rental charges for 14 days, if lab is rented.		
Time Frame (to get validated analysis)	Contractually 30 to 40 days	Real-time to several hours		
Prioritized Data Uses	- confirmation - toxicology/risk assessment - all other program activities e.g., ROD, rem-design, etc. - PRP determination - litigation	- presence or absence of contaminants - preliminary site characterization and screening - engineering design - temporary alternatives - removal action (resulting in alternate water supply, fencing, etc.) - health and safety		
Limitations	- tentative ID of non HSL parameters - sufficient time required for package validation - high cost	- tentative ID of all parameters - techniques/instruments not very sophisticated - loss of instrument sensitivity during mobilization - results may not support legal issues		
Technician/Analyst Requirements	BS chemist/well trained	- preferably BS chemist with sufficient training - should be capable of interpreting field data		

chemical analyses can be done on matrices such as soil, liquid, sludge, water, and air samples. Typically, results from analysis can be made available within 4 to 24 hours after sampling. The advantages of employing on-site mobile laboratories (over traditional off-site, fixed-base laboratories) include

- Potential cost savings
- Greatly reduced analytical time
- An ability to modify sampling strategies on an almost instantaneous basis
- A potential decrease in the number of samples being sent to fixed-base laboratories
- Assistance to the geological decision-making process for determining the location of boreholes/monitoring wells and the most effective depth of monitoring wells
- Rapid determination of the presence or absence of contaminants
- Avoidance of concerns such as holding times and packing and shipping of samples

Potential disadvantages of employing on-site mobile laboratories include the following:

- If samples are not ready, the costs are still incurred.
- The utility of the data for litigation purposes is questionable.

The cost of employing a mobile laboratory is dependent upon several factors including the time that a laboratory must remain on site, the distance a laboratory must be transported to a site, and the equipment, services, and personnel required for the characterization activity. The QA/QC protocols employed and the level of documentation provided by mobile laboratory services are typically negotiable and defined contractually.

Unlike fixed-base laboratory analyses, costs for mobile laboratory work are not generally calculated on a cost-per-sample basis. Costs are determined by the number of days the laboratory is employed plus a fixed fee for transportation of the laboratory. These costs decrease as the duration of use increases and the rental rate per day is higher if the mobile laboratory is hired for a shorter duration. Accordingly, the cost-effectiveness of employing mobile laboratories (over fixed-base) is directly linked to the rate at which site samples can be generated for analysis. Although site characterization using mobile laboratories is generally less expensive, this cost advantage can easily be lost due to poor planning or unexpected delays in sampling activity while the mobile laboratory is on site.

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1. "Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA," OSWER Directive 9335-3-01, March 1988.

2. "Data Quality Objectives for Remedial Response Activities," EPA/540/G-87/003, March 1987.

3. "Proceedings of the Third Annual Symposium on Solid Waste Testing and Quality Assurance," Environmental Protection Agency, Washington, D.C., July 1987.

ENZYME IMMUNOASSAY FOR THE QUANTITATION OF AN ALKALINE PROTEASE IN AIRBORNE SAMPLES

Larry S. Miller, Victor Moore, Abbie Wardwell,
Michelle Buchwalter, and Laurence A. Smith+
Battelle, Biotechnology Section, 505 King Avenue, Columbus, OH 43201
+The Procter & Gamble Company, Ivorydale Technical Center,
5299 Spring Grove Avenue, Cincinnati, OH 45217

ABSTRACT

Alkaline proteases are used as additives in detergent products. Because they are allergenic to workers in manufacturing areas, the work environment is monitored for airborne levels of these enzymes. A sensitive and specific inhibition enzyme immunoassay (IEIA) was developed for the quantitation of an alkaline protease, subtilisin. This IEIA had a detection limit of 1 ng/ml (36.7 pM), a response range of 1-50 ng/ml, no crossreactivity with other microbial proteases, and excellent inter- and intra- assay reproducibility. The presence of detergent product or environmental materials did not interfere with the method. Air filter samples from manufacturing areas producing subtilisin-containing detergent product were analyzed for antigenic and enzymatic activities of the alkaline protease. A high correlation coefficient of 0.893 was obtained between these methods. By the IEIA, the air samples were found to contain 1-18 ng/ml of subtilisin with a mean of 7.2 ng/ml and it was possible to detect 0.15 ng subtilisin protein per cubic meter of air. In addition to sensitivity and specificity, the IEIA also circumvented problems associated with the reference method such as interference by other environmental proteases and sample color.

Key words: immunoassay, environmental monitoring, air samples, allergens

INTRODUCTION

Environmental monitoring for low levels of toxic or hazardous compounds in air, water, and soil samples has been performed using sophisticated analytical chemistry techniques. Although these methods can detect substances in the ppm to ppb range, they usually require complex equipment and need extensive sample preparation. In addition, they are limited in number or type of samples and are costly to perform for routine analysis.

In some cases, immunoassays may offer an alternative to conventional analytical chemistry techniques that are now used for environmental analysis. Immunoassays employ specific antibodies that can detect compounds in the ppb to ppt range. Because of the antibody specificity, it is possible to analyze a complex mixture with only minimal sample preparation, to detect several substances in one sample, and to use small sample volumes (0.5 to 1.0 ml).

Subtilisin Carlsberg (EC 3.4.4.16) is an alkaline protease from Bacillus licheniformis which has properties useful for detergent products (1). It is necessary to control airborne levels of this enzyme in manufacturing sites because of its allergenicity as reported by Pepys et al (2). An enzyme activity assay has been developed for this purpose (3). However, this procedure is affected by interfering substances, the stability of subtilisin in the detergent product, and the presence of other proteases in the air samples from environmental microorganisms.

An immunoassay approach offers potential advantages over enzyme assays for evaluation of air samples because of their specificity and sensitivity. This study reports the development and validation of an IEIA for subtilisin and its application to the analysis of air samples for this allergen.

DEVELOPMENT OF AN INHIBITION ENZYME IMMUNOASSAY FOR SUBTILISIN

Rabbit anti-subtilisin sera were prepared and used to develop an inhibition enzyme immunoassay (IEIA). The IEIA is outlined in Figure 1 and is a modification of the indirect enzyme immunoassay described by Voller et al (4). Diluted antiserum was mixed with an equal volume of the sample or subtilisin standards. After an overnight incubation to allow subtilisin to react with the antibody binding sites, this solution was added to microwells containing subtilisin adsorbed to the plastic surface. Free antibody binding sites would bind to the immobilized subtilisin while subtilisin-antibody complexes would be inhibited. The level of rabbit anti-cellulase antibody that was bound to the solid-phase subtilisin was

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determined by adding goat anti-rabbit IgG, alkaline phosphatase conjugate to the microwell. After an incubation step, the excess conjugate was removed by washing the microwell. Para-nitrophenylphosphate was added and this chromogenic substrate was converted to a yellow product by the alkaline phosphatase bound to the microwell. The absorbance at 405 nm was determined using a colorimeter that was designed to read 96 microwell plates (MicroELISA Autoreader, Dynatech). The concentration of subtilisin in a sample was determined from an inhibition curve. For the IEIA, absorbance values for the microwell solution was inversely proportional to the concentration of subtilisin in the sample or standard solution.

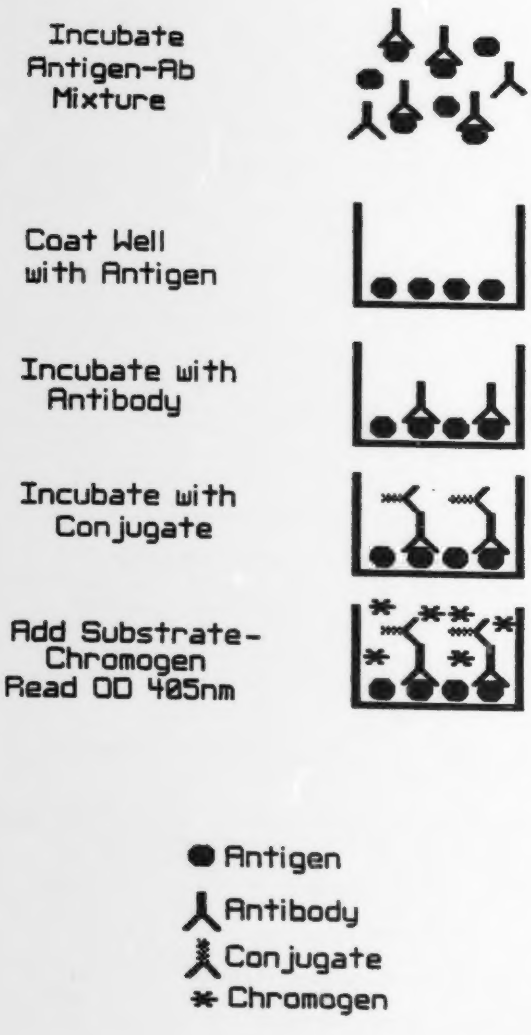

Figure 1. Inhibition enzyme immunoassay for subtilisin.

An inhibition curve for the IEIA was developed using a 1:20,000 dilution of the anti-subtilisin sera and concentrations of subtilisin from 1-100 ng/ml. This assay was found to have a limit of detection of 1 ng subtilisin protein/ml and a response range of 1-50 ng/ml (figure 2). The total assay time was approximately 20 hrs which included 16 hrs for the initial incubation of sample and diluted antisera. This schedule allowed for the preparation of multiple samples on the first day and the completion of the test and data analysis on the following day.

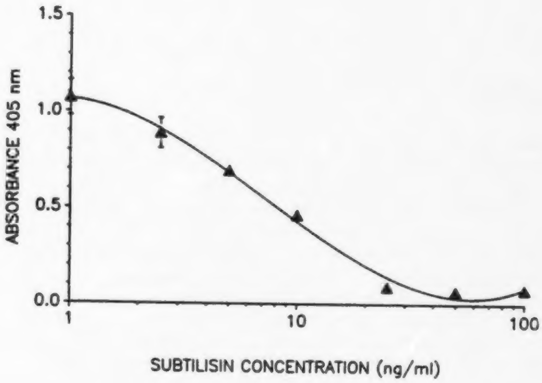

Figure 2. Inhibition curve for the subtilisin IEIA. Each point represents the mean of triplicate samples and the standard deviation by error bars.

The specificity of the anti-subtilisin sera was evaluated using other microbial proteases (1-1000 ng protein/ml) in the IEIA. They included thermolysin, proteinase K, pronase, and newlase. The concentration of antigen required for 50% inhibition (ID50) was determined and only subtilisin was inhibitory (ID50 42 ng/ml). The other microbial proteases did not demonstrate inhibitory activity at any concentration (ID50 >1000 ng/ml). This demonstrated that the antibodies used in the IEIA were highly specific for subtilisin.

IEIA VALIDATION STUDIES

These studies were performed to assess the effects of various conditions on the inhibition curve for the subtilisin IEIA. Any factors found to affect the IEIA were assessed and measures to remove or control their effect were developed.

Anionic detergents have been shown to have an inhibitory effect on immunoassays (5). Detergent products containing anionic and other surfactants were evaluated at 0.001%, 0.01%, or 0.1% in the IEIA using 1-100 ng/ml concentrations of subtilisin. These conditions represent a 100 to 10,000 fold excess of detergent product to subtilisin by weight. The inhibition curve was not affected by the granular detergent product and was similar to the inhibition curve in figure 2. The surfactants in the detergent product may have had no effect on the IEIA due to the presence of bovine serum albumin which has binding sites for long alkyl chain molecules including sodium dodecyl sulfate (6).

Recovery studies were performed to determine if there were any interactions between air sample components and subtilisin. Material was eluted from 12 air filters and subtilisin was added to an approximate final concentration of 10 ng/ml. The antigenic activity of subtilisin added to the air sample solutions was compared to a buffer control. A 0.7 to 1.1 fold difference in antigen activity between the air sample and the control was obtained with an average ratio of 0.8.

The source of this variation for the recovery studies was examined. The material that was eluted from the air samples were diluted to determine if an interfering substance in the sample matrix would lose its effect. The antigenic activity demonstrated excellent proportionality for each two fold dilution and so this effect did not appear to be due to components in the air sample solution. In addition, the effect of the subtilisin protease activity on the IEIA was evaluated and did not affect the inhibition curve. Next, the samples were treated with a 0.45 m membrane filter to evaluate if particles in the air samples may be the source of this difference. The removal of particles by filtering the solution demonstrated a 20-30% loss in activity and appeared to be the source of this difference. This situation was corrected by increasing the salt concentration of the elution buffer to 0.5 M to facilitate desorption of subtilisin from the air particles.

The reproducibility of the subtilisin IEIA was determined from inter- and intra- assay studies. Interassay reproducibility was evaluated by repeating the inhibition curve for the IEIA on three consecutive days while the intraassay reproducibility was determined with triplicate inhibition curves on the same day. The IEIA was highly reproducible for both inter- and intra-assay studies with <10% coefficient of variation. The inhibition curves were similar to figure 2.

ANALYSIS OF AIR SAMPLES FOR SUBTISIN BY THE IEIA

Air samples from manufacturing sites were collected and evaluated for subtilisin content by the IEIA and a reference method for subtilisin enzyme activity (7). Air samples were collected on glass fiber filters for 120 minutes with a total air volume ranging from 88 to 100 m^3. Material was eluted from the glass fiber filter by rapidly mixing with 20 ml of buffer containing 0.5 M sodium chloride, 0.02 M Tris, 0.01% Tween 20, 0.1% bovine serum albumin, 0.02% sodium azide, 0.001 M calcium chloride, 0.001 M phenylboronic acid, and 0.001 M sodium thiosulfate at pH 8.0. The fragmented filter particles were separated from the solution by centrifugation at 2000g for 10 min at 4°C. The supernatant was stored at 4°C and used for subtilisin analysis. The enzyme assay (7) was performed by adding sample or standards to a solution of 20 mM Tris buffer, pH 8.0 containing 2mM succinyl-ala-ala-pro-phe-paranitroanalide. Subtilisin or other serine protease would convert this chromogenic substrate to a yellow product that was detected spectrophotometrically at 405 nm.

The subtilisin content of 20 air samples was determined for antigenic activity by the IEIA and for enzyme activity by the reference method. The values ranged from 4.8-18.4 ng/ml for the enzyme assay and 0-18.0 ng/ml for the IEIA with means of 10.7 ng/ml and 7.2 ng/ml, respectively. For the IEIA data, these concentrations were equivalent to 14 to 360 ng subtilisin per filter pad or 0.15 to 3.79 ng/m^3 air. A high correlation coefficient was obtained between these methods (r=0.893). However, the linear regression line slope (0.8) indicated generally higher values for the antigenic than the enzymatic activity (figure 3A). Furthermore, the y-intercept for the enzyme activity assay at 7 ng/ml indicated a bias in this method. Therefore, the enzyme assays was evaluated for sources of these differences.

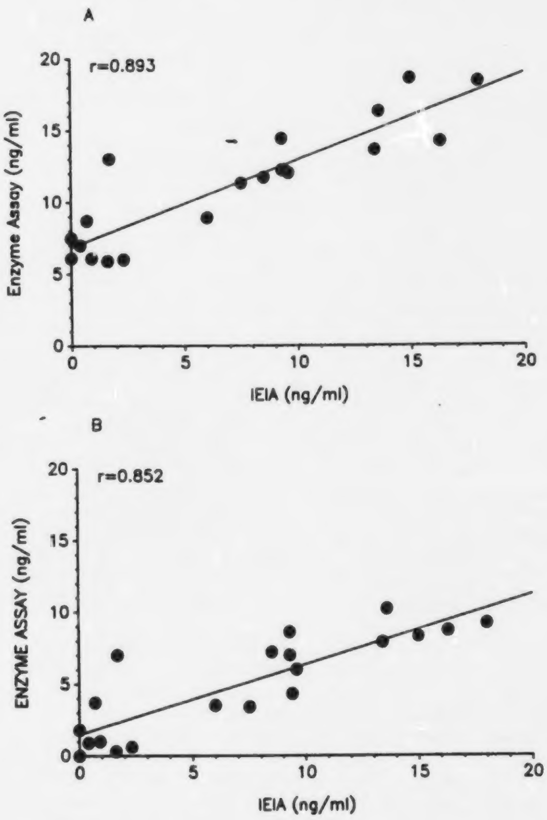

Figure 3. Correlative studies for the subtilisin IEIA and enzyme assay. Initial data is in panel A. Enzyme assay results corrected for sample color and endogenous sample protease activity in panel B.

Some of the air samples had a color ranging from yellow to dark gray which produced absorbance values as high as 0.117. Since the sample color interfered with the enzyme assay, these values were corrected. This correction was not necessary for the IEIA because the air sample solution was washed from the reaction before determining the absorbance.

The air samples were found to contain proteolytic enzymes that was not from the detergent product. Air samples from a manufacturing site not containing subtilisin were collected and analyzed for ambient protease activity. The mean enzyme activity of these samples was 4.5 ng/ml with a range of 3.9 to 5.0 ng/ml. The enzyme activity assay uses a chromogenic substrate reagent which is reactive with subtilisin and other proteases. Analysis of these samples by the subtilisin IEIA revealed that there was no detectable subtilisin antigenic activity. The source of these proteases may be environmental microorganisms that occur in the air.

Correcting the enzyme assay data for sample color and background enzyme activity, it was possible to decrease the variation in the data between the enzyme assay and IEIA methods. The correlation coefficient remained high (r=0.852) and the intercept for the regression line was moved to near the origin (figure 3B). The line slope (0.67) suggests that there is more detectable antigenic activity in the samples than enzymatic activity. This bias may be attributed to these assays detecting two different properties of the subtilisin molecule, its antigenic and enzymatic activities. The IEIA can detect degradation products as well as intact subtilisin while the enzyme activity assay will detect only enzymatically active forms of subtilisin.

SUMMARY AND CONCLUSIONS

Subtilisin, a microbial protease, is used in detergent products (1) and can result in allergic reactions upon exposure of workers in manufacturing areas (2). Although this has been controlled by reducing dust levels, it is necessary to monitor the air for this enzyme. An IEIA for subtilisin was developed for the analysis of air samples. This highly reproducible assay has a sensitivity of 1 ng/ml and does not detect other microbial proteases. Validation studies of this method demonstrated that it detected subtilisin in detergent product and the air sample matrix.

The utility of the IEIA for subtilisin quantitation was determined from comparative studies with air samples from detergent manufacturing sites. A high correlation coefficient (r=0.852) was obtained between the IEIA and a reference method for subtilisin enzyme activity. It was found that the IEIA could detect subtilisin at levels as low as 0.15 ng per cubic meter of air. This level of detection and other characteristics of this assay are comparable to those reported for radioimmunoassays of other protein allergens, esperase (8) and papain (9). However, the enzyme immunoassay offers advantages over radioimmunoassays in that special handling and reagent stability are not problems. The subtilisin IEIA was easy to use, required only 300 ul of sample, used simple sample preparation to transfer the dust to solution, and analyzed simultaneously 23 samples and standards in triplicate.

There are many potential applications of immunoassays for environmental monitoring. For subtilisin and other airborne allergenic proteins, immunoassays provide an approach for their detection in the manufacturing environment which is not feasible by standard chemical methods. This approach is also applicable to small organic compounds such as pesticides, herbicides, insecticides, and fungicides (10). Other immunoassays formats can be used to automate the analysis of large numbers of samples, to evaluate one sample for several compounds, and to perform near real-time analysis at a disposal or storage sites.

ACKNOWLEDGEMENT

This study was supported by The Procter & Gamble Company. Secretarial assistance was provided by Shan Wolfington and Sandra Jennings. We wish to thank Dr. Jeanette van Emon and Dr. P. Albro for their comments.

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GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC ANALYSIS OF TARGET AIR TOXICS AT REMEDIAL HAZARDOUS WASTE SITES

D.W. Hodgson[a], B.G. Miller, R.A. Ross and T.S.Viswanathan[b]
NSI Technology Services Corporation
400 State Ave., Gateway Center Tower II, Suite 311
Kansas City, KS 66101

R.D. Kleopfer[a] and W.W. Bunn
U.S. EPA Laboratory
25 Funston Rd.
Kansas City, KS 66115

ABSTRACT

GC and GC/MS analytical methods were used for the analysis of air-toxics at two Superfund waste sites. Data was utilized for ambient air monitoring and for supporting remedial actions. Ambient air samples from the waste site, collected on Tenax cartridges, were analyzed by using the modified Gas Chromatography-Mass Spectrometry (GC/MS) method, TO-1 (1). The compounds of interest, chloroform and carbon tetrachloride, were detected at the 1 ng level in most samples. To support remedial actions, Air Stripper water samples and Vapor Extraction System (VES) vapor samples from the site were analyzed by direct injection on an electron capture gas chromatograph at a laboratory close to the remedial site. Tedlar bags and gas syringes were used as vapor sample collection containers. Analytical results for these samples ranged from the detection limit (.3 mg/m^3) to 19 mg/m^3 for chloroform and 1.2 to 910 mg/m^3 for carbon tetrachloride. Problems encountered in sampling and analysis, data quality assessment procedures, and logistics in providing fast turnaround analytical results are discussed along with other related issues.

INTRODUCTION

Air quality, both indoor and outdoor is increasingly becoming an important issue for the general public. To combat outdoor pollution, governments around the world have adopted laws and regulations that control emissions from a number of static and dynamic sources such as those from coal-fired power plants, manufacturing plants, automobiles and even fireplaces from individual homes. A different but increasingly common source of air pollution is one that results from cleanup efforts aimed at the remediation of known hazardous waste sites. This type of pollution is often a local event of short duration that differs significantly from such events as the Bhopal, India incident or the Seveso, Italy incident in that the emissions can be controlled. Cleanup activities at the Superfund sites managed by the Environmental Protection Agency (EPA) are accompanied by well-planned air-monitoring programs designed to safeguard the short and long-term health of workers, scientists and residents in the vicinity of the waste-sites. An example of such a program is the monitoring of air-samples from dioxin sites in eastern Missouri. During cleanup, ambient air samples are collected on polyurethane foam cartridges and analyzed for 2,3,7,8-tetrachlorodibenzodioxin (2). In this case, the pollutant is not volatile, and the air pollution is, for the most part, caused by construction machinery which releases dust particles containing the bound pollutant into the air.

One of the remediation projects, supported analytically by the recently formed Environmental Services Assistance Team (ESAT - An EPA contractor providing technical and analytical support for Superfund activities), was concerned with the restoration of clean ground water to two communities in central Nebraska. The ground water, contaminated with the fumigants chloroform and carbon tetrachloride, was cleaned-up by air stripping. Soil gas containing the contaminants was removed by using a Vapor Extraction System (VES). The concentrations of the target toxics in the groundwater before, during and after treatment, and the VES emissions were monitored by ESAT chemists in cooperation with EPA and other EPA-contractors. This paper summarizes the analytical methodology, quality assurance procedures, logistics and other considerations involved in providing the required analytical support for this complex remediation effort.

PROJECT DESCRIPTION

The project at the Waverly, Nebraska site consisted of analyzing VES vapor samples and air-stripper process water samples for chloroform and carbon tetrachloride using a gas chromatography/electron capture (GC/ECD)

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[a] Current Address:
Hall-Kimbrell Environmental Services
4848 W. 15th Street
Lawrence, KS 66044-0307

[b] Address correspondence to this author

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technique. To minimize blank-contamination and to provide data in a timely manner the analysis was not performed at the waste-site but in a nearby laboratory. Samples were collected in the field and delivered to the laboratory by an EPA-contractor. Results were reviewed and reported to the designated project managers by telephone. Support to EPA for this project was provided by NSI from 1-20-88 to 2-19-88.

The ambient air-monitoring project at the Murdoch, NE and Waverly, NE sites consisted of analyzing Tenax sorbent cartridges through which a known volume of ambient air had been drawn. The pollutants, $CHCl_3$ and CCl_4, were desorbed thermally and analyzed using a gas chromatography/mass spectrometry (GC/MS) technique. Support to EPA for this project was completed in July '88.

The steps involved in ESAT's analytical support consisted of the following:

1. Selection of appropriate analytical methods and the development of a Quality Assurance Project Plan for the Waverly, NE project and a Standard Operating Procedure for analytical support of the Murdoch, NE project.

2. Performance of laboratory analysis using methods identified in step 1.

3. Review of analytical data by analysts and reporting by telephone for rapid turnaround.

4. Detailed follow-up review of analytical data to assess precision, accuracy, completeness and other performance criteria associated with the analytical methods.

5. Recommendations for future field or on-site analytical support.

EXPERIMENTAL

The GC/ECD analyses were performed using a Hewlett Packard (HP) 5890 gas chromatograph equipped with a HP 10 MByte hard disk drive, HP model 3393A integrator, and a HP model 7634A autosampler. The EPA Method no. 501.2, "Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction" was used with the following modifications:

1. A 30 m DB-Wax (J&W Scientific) megabore (0.53 mm I.D.) capillary column of 1.0 micrometer film thickness was used for chromatographic separation. Chromatography was done isothermally at 40°C using argon /5%-methane as the carrier gas. The GC run times were typically 3.5 minutes in length.

2. A separate, four point calibration curve was developed for each class of water samples tested. The calibration ranges consisted of the following concentrations (micrograms/liter): For effluent water, CHCl3 - 0.2 to 0.7; CCl_4 - 0.4 to 1.4; for midprocess water, $CHCl_3$ - 1.0 to 3.4; CCl_4 - 10 to 34; for influent water, $CHCl_3$ - 18 to 60; CCl_4 - 900 to 3000.

3. For vapor samples, 15 to 40 microliters of 1 ppm $CHCl_3$ and 1 ppm CCl_4 gas-phase standards were injected to construct the 4 point calibration curve. The calibration range was 80 pg to 260 pg for $CHCl_3$ and 100 pg to 320 pg for CCl_4. Static dilution bottles for diluting either vapor samples or gaseous standards were unavailable to the analysts at the field laboratory.

4. Dilution of water samples with organic-free, distilled, deionized water was employed to overcome the constraints of a limited calibration range for samples that exceeded the upper calibration range.

All the GC/ECD measurements reported in this article were performed at the Nebraska Department of Environmental Control (NDEC) laboratory in Lincoln, NE. To support this project, the NDEC laboratory kindly provided counter and hood space, electricity and access to their facility outside the normal working hours. The equipment, and all other supplies including gas cylinders, syringes, glassware, etc. were transported from the EPA regional laboratory in Kansas City, KS to the Lincoln, NE location.

ANALYTICAL STANDARDS

Analytical standards of chloroform (10 micrograms/liter) and carbon tetrachloride (5 micrograms/liter) in methanol were obtained from the NSI-operated EPA Analytical Standards Repository in Research Triangle Park, NC. A vapor phase analytical standard mixture of chloroform and carbon tetrachloride (1 ppm v/v each) in nitrogen was obtained from Scott Specialty Gases.

SAMPLING AND ANALYSIS OF VAPOR EXTRACTION SYSTEM VAPOR SAMPLES

Vapor phase samples collected in Tedlar bags or 50 cc Luerlock glass gas-syringes with a stainless steel ball valve were employed for sampling. The syringe was used in the later part of the project since the VES sampling ports were at or below atmospheric pressure and the samples collected in collapsible Tedlar bags did not yield analytically reproducible results. Either of these methods were preferred over sorbent absorption techniques due to the high concentration of the analytes and the speed of sampling with Tedlar bags and/or syringes. Also, charcoal, Tenax and XAD sorbent cartridges were not used since the desorption of analytes from these tubes and subsequent analysis requires a relatively long period of time. In addition, some protocols require three separate analyses; one each for the front particulate filter, the front sorbent and the back sorbent. This would have tripled the analysis time.

Vapor samples collected in Tedlar bags or gas syringes were transported to the lab at ambient temperature and analyzed by injecting an appropriate volume of sample (< 1 microliter to 500 microliters) directly into the gas chromatograph. The injection volume was adjusted effectively to bring the analyte GC/ECD response within the calibration range. Response factors (RF) in units of picogram of analyte standard injected per unit GC peak area were defined; these were used to calculate the sample concentration using the following equation :

$$C_a = (A_s * RF) / V_s \qquad (1)$$

where:

C_a = concentration of analyte in pg/microliter or mg/cu.m. units
A_s = GC peak area for sample
V_s = Volume of air injected (microliters)
RF = Response factor for analyte (pg/A)

SAMPLING AND ANALYSIS OF WATER SAMPLES

Water samples were collected in 40 ml vials with teflon-lined screw caps and shipped to the laboratory in ice filled coolers. Ten milliliters of the sample were extracted with two milliliters of pentane; one microliter of the extract was injected into the gas chromatograph for analysis.

SAMPLING AND ANALYSIS OF AMBIENT AIR

Ambient air samples were collected by drawing a known volume of air through clean Tenax cartridges. The thermal desorption and mass spectral analyses were performed by using a Finnigan 4000 GC/MS/DS system interfaced to a Tekmar 5010 thermal desorber.

Tenax cartridges were fortified with the internal standard d_4-1,2-dichloroethane (for use in quantitative analysis) by injection into the desorber gas stream. The pollutants and the internal standards were prepurged to remove water from the sorbent at 40°C using a helium flow of 15 ml/min. The pollutants and the internal standards were desorbed thermally by heating the cartridges to 190°C using a helium flow of 15 ml/min. and trapped using a liquid-nitrogen cryogenic trap at -125°C inside the Tekmar 5010 desorber. The analytes were subsequently desorbed thermally at a lower capillary column-compatible helium flow rate of 1-2 ml/minute and were trapped again on a cryogenic trap at -125°C at the capillary interface unit near the head of the capillary column. A quick injection of the trapped analytes was made into the GC column by heating the trap at the interface unit rapidly to 250°C. The analytes were separated on a 50 m DB-5 (J&W Scientific) GC capillary column (0.32 mm I.D. and 1 micrometer film thickness) using the following conditions: Initial temperature: 30°C for four minutes; temperature programming: 6°C/minute ramp to 90°C followed by a second ramp at 25°C/minute to 200°C to prepare the column for the next run.

All calibration and internal standards were prepared by vaporizing a known amount of high purity, liquid phase standard material in a 2 liter gas dilution bottle equipped with a mini-inert valve. The concentration of each compound was calculated from the following equation :

$$C = (d * I) / V \qquad (2)$$

where:

C = compound concentration (ng/microliter)
d = density of compound (g/ml)
I = amount injected (microliters) into the Static Dilution Bottle, and
V = Volume of Static Dilution Bottle (liters)

The calibrations were performed by absorbing the appropriate vapor phase analytical standards and the internal standard onto a blank Tenax cartridge in the same manner that the internal standard was added to the sample cartridges prior to analysis. Calibration curves consisting of a blank and two concentration levels of analytes were employed for initial calibration. Each day samples were analyzed, the calibration factors were verified at one concentration level.

RESULTS

A. GC Analysis

A total of 123 samples consisting of 56 vapor samples and 67 water samples were analyzed for chloroform and carbon tetrachloride during a four week period from 1-22-88 to 2-19-88 in support of remedial efforts at the Waverly, NE Superfund site. The analysis of 123 samples required 1057 separate injections including those needed for the multi-point calibration at multiple calibration ranges for each of the two matrices, laboratory method blank for the two matrices, matrix spike, matrix spike duplicates, field duplicates, laboratory duplicates, sample dilutions, etc. The analytical results for the samples varied from none detected (the lowest detection limits that were reported are shown below in parentheses) to very high concentration levels:

For water:

$CHCl_3$ from: (0.2) to 170 micrograms/liter
CCl_4 from: (0.1) to 6400 micrograms/liter

For vapor:

$CHCl_3$: from (0.1 to 0.4) to 23 mg/m^3
CCl_4: from (0.2) to 910 mg/m^3

The following performance factors were assessed for determining data quality for the project:

1. GC Retention Time Stability

This factor affects the ability to identify the analyte qualitatively. From the calibration standard analysis runs, the following retention time (RT) data were collected. The mean RT, standard deviation (s) and the percent relative standard deviation (RSD) from 16 data points collected between 1-23-88 and 2-18-88 for air analyses were:

For $CHCl_3$:

RT = 0.858 min.; s = 0.004 min.; RSD = 0.46%

For CCl_4:

RT = 1.971 min.; s = 0.009 min.; RSD = 0.47%

2. Method Blank Results

Twelve of fourteen water method blanks, which consisted of distilled deionized water, contained low levels of $CHCl_3$ (0.1 to 0.4 micrograms/liter) and CCl_4 (0.1 micrograms/liter). The remaining two water method blanks showed elevated levels of $CHCl_3$ (3.3 to 3.6 micrograms/liter) and CCl_4 (1.2 to 1.6 micrograms/liter). The laboratory method blanks for vapor samples, which consisted of 50 to 500 microliters of air obtained from outside the laboratory, were mostly free of analytes. Small amounts of chloroform (0.1 & 0.2 mg/cu.m.) and CCl_4 (0.1 & 0.7 mg/cu.m.) were observed in 2 of the nine blanks. At least one matrix specific method blank was analyzed for each day water or air samples were tested. Detection limit thresholds for the analysis were calculated as twice the level found in the blank. Positive values for analytes below the threshold were reported as not detected. Sample results above the threshold were reported without correction for blank concentrations.

3. Reproducibility of Response Factors

Instrument responses for $CHCl_3$ and CCl_4 were linear over the short ranges of concentrations described in an earlier section. The response was non-linear over wider concentration ranges. The response factor stability over the project period was excellent. For all the calibration runs performed during the project, the percent relative standard deviation of the response factors varied from 19% to 22% for $CHCl_3$ and from 23% to 26% for CCl_4.

4. Reproducibility of Analysis

Duplicate determinations were performed on 16 water and 15 vapor samples, a minimum of one duplicate analysis for each day water or air samples were tested. This represents a frequency of more than 20%. The duplicate results for $CHCl_3$ and CCl_4 in water samples are shown in Tables I and II respectively. The numbers in parentheses are detection limits. The percent difference (%D) for duplicate results was calculated using the following equation:

$$(\%D) = |200 * (S_1-S_2)/(S_1+S_2)| \qquad (3)$$

where S_1 and S_2 are the results of replicate analysis. The %D is generally lower at concentrations >5 micrograms/liter. The mean %D for vapor analysis, based on 13 determinations, was 17% for chloroform and 38% for carbon tetrachloride.

TABLE I

REPRODUCIBILITY OF $CHCL_3$
RESULTS IN WATER SAMPLES
(micrograms/liter)

Number	S_1	S_2	%D
1	16	19	16
2	19	12	37
3	0.3	0.7	130
4	29	22	24
5	1.9	1.0	49
6	0.3	0.5	67
7	21	21	0
8	(0.3)	(0.3)	0
9	1.9	2.0	5
10	23	20	13
11	0.6	(0.1)	--
12	19	19	0
13	20	3.9	81
14	(0.3)	(0.3)	0
15	44	41	7
16	44	43	2

n = 15
mean %D = 29
S.D. = 38

TABLE II

REPRODUCIBILITY OF CCL_4
RESULTS IN WATER SAMPLES
(micrograms/liter)

Number	S_1	S_2	%D
1	44	60	36
2	1260	1190	6
3	(3)	(3)	0
4	2970	3300	11
5	26	33	27
6	0.5	0.2	60
7	2240	2360	5
8	(1.8)	(1.8)	0
9	37	42	14
10	2540	2240	12
11	0.9	0.9	0
12	2450	2340	5
13	3140	395	87
14	1.8	2.0	11
15	3020	4240	41
16	6380	6290	1

n = 16
mean %D = 20
S.D. = 25

5. Spike Recovery

A total of eleven water and eight vapor samples, representing a frequency of 16% and 14%, respectively, were spiked and analyzed. The amount spiked into water samples varied from 25 to 563 micrograms/liter for chloroform and from 20 to 2000 micrograms/liter for CCl_4. The eleven water samples contained from 1 to 44 micrograms/liter of chloroform and from 1 to 6380 micrograms/liter of CCl_4 before spiking. The recovery of the spiked analytes, in valid experiments, varied from 0% to 150% for chloroform and 0% to 145% for CCl_4 with the following statistics:

$CHCl_3$: n = 9; mean = 83%; S.D. = 36%
CCl_4: n = 10; mean = 90%; S.D. = 49%

The eight vapor samples contained chloroform from 0.1 to 23 mg/m^3 and CCl_4 from 0.8 to 448 mg/m^3 before spiking. The amount spiked into the samples varied from 38 to 500 mg/m^3 for chloroform and from 60 to 2000 mg/m^3 for CCl_4. Since static dilution bottles were unavailable, matrix spikes were performed by injecting small volumes (<25 microliters) of methanolic $CHCl_3$ and CCl_4 standards directly into the sample syringe. Incomplete vaporization of spiked analytes cannot be ruled out under these conditions. The recovery of spiked analytes varied from 16% to 121% for $CHCl_3$ and 7% to 329% for CCl_4 with the following statistics:

$CHCl_3$: n = 7; mean = 60%; S.D. = 33%
CCl_4: n = 7; mean = 94%; S.D. = 112%

6. Performance Evaluation Audits

Two water audits were performed during this project. The true value of CCl_4 in both audit samples was 20.4 micrograms/liter. The observed values were 24.7 and 22.2 micrograms/liter, which translates to % recoveries of 121% and 109%, respectively. The true value of chloroform in both audit samples was 20.2 micrograms/liter. The observed values, 73 and 162 micrograms/liter, were much higher. A co-eluting interference which was partially resolved on the column, as evidenced by GC peak broadening, led to higher analytical results for chloroform. Four other chlorinated hydrocarbons were also present in the audit sample. No reference standards were available on-site to determine the identity of the co-eluting peak which was not observed in the analysis of actual samples.

7. Overall Assessment of GC Data Quality and Analytical Support

The detection limits of 5 micrograms/liter for water samples and 1 micrograms/m^3 in vapor samples for $CHCl_3$ and CCl_4 were easily accomplished. The required analytical turnaround times of 8 hours for vapor samples and 48 hours for water samples were also met. The objective of >90% completeness was met as well. With regard to precision, the data was quite variable for both water and vapor samples. The highest degree of variability was observed for sample concentrations near the detection limits, as would be expected. The accuracy of the GC analytical results was estimated at +/- 150%, which was within the target range of +/- 200%. A number of factors inherent in the method created the significant variation observed in the data. Some of these are listed below:

1. Lack of stability of water samples.
2. Large dilution factors for some water samples.
3. Wide range of injection volumes for vapor samples required to have the instrument response within the calibration range.
4. Difficulty in spiking and withdrawing vapor samples from the 50 ml glass syringe containers.

B. GC/MS ANALYSIS

Over 125 ambient air samples collected in Tenax cartridges have been analyzed to date for chloroform and carbon tetrachloride using the modified method TO-1 in support of ongoing remedial projects. The following performance characteristics were observed for this method over a one week period:

1. Calibration Factors

Relative response factors for analytes with respect to the internal standard, d_4-1,2-dichloroethane were defined as follows:

$$RRF = (A_a/A_{is}) * (W_{is}/W_a) \qquad (4)$$

where:

RRF = relative response factor for $CHCl_3$ or CCl_4
A_a = area for the analyte quantitation ion; m/z 83 for $CHCl_3$ and m/z 117 for CCl_4
A_{is} = area for the internal standard quantitation ion of m/z 65
W_{is} = amount (ng) of internal standard, and
W_a = amount (ng) of analyte

The relative response factors determined daily over a one week period varied substantially. The following statistics were observed for eleven such determinations:

Analyte :	$CHCl_3$	CCl_4
Mean RRF :	1.38	1.24
Standard Deviation:	0.67	0.98
Percent Relative Standard Deviation:	49%	79%

The mean value and standard deviation of the absolute response for 50 ng of the internal standard were 16803 area units and 12703 area units, respectively. Sixteen determinations were made.

2. Retention Time Stability

The retention time (RT) stability for the internal standard and the analytes was substantially worse for the GC/MS method than for the GC method as shown below:

Compound	: Internal Standard	$CHCl_3$	CCl_4
No. of analyses :	16	12	12
Mean RT (s) :	235	200	246
Standard deviation:	21	14	18
Percent Relative standard deviation:	8.9	7.0	7.3

The manual trigger mechanism employed for coordinating three events, sample injection by the Tekmar 5010, the start of the GC run, and the start of the MS data acquisition contributed somewhat to the observed scatter in the retention times. The major contributor, however, was the poorly designed GC oven-sub-ambient temperature controller. Since automated data reduction procedures required a narrow RT window, analyte identification using mass spectral match and quantitations were done manually.

PROBLEMS

The analytical results for chloroform and carbon tetrachloride for vapor samples collected in Tedlar bags were not reproducible. These compounds had a tendency to adhere strongly to the walls of the bag. Agitation of the bags led to laboratory sub-samples with higher values. Variations up to 700% were observed for seven replicate determinations with higher values corresponding to higher degrees of agitation. Higher results were also observed when the samples collected outdoors in the cold winter months were allowed to warm up to room temperatures. Additional problems were encountered in performing matrix spike recovery determinations. Consequently, Tedlar bags were discontinued in favor of glass syringes as vapor sampling devices. One drawback with the syringes, however, was the collection of an oil/water emulsion in the syringe ball valve, which occasionally contaminated the analytical syringes.

A number of administrative problems needed to be resolved for providing the field analytical support. For example, the transportation of the GC equipped with a radioactive Nickel-63 source in the electron capture detector across the state lines required prior permission from the state government agencies. The use of versatile automated GC equipment enabled the one-person field analytical crew to perform a number of tasks simultaneously. Projects of this type require experienced, adaptable and versatile chemists who can operate without much supervision and are also capable of reviewing their own data for quality and usability within the limited analytical turnaround time.

A number of analytical problems were observed in the analysis of Tenax samples. The clogging of capillary columns by ice (due to incomplete removal of moisture during the prepurge step) and/or particulates from the cartridge was a serious problem. Using the system described above, one large tank of liquid nitrogen is required for the analysis of approximately 30 samples.

CONCLUSION

From our experience, we can conclude that providing sampling and analytical support for air monitoring is far more complex than it may appear. The lack of availability of gaseous standards, inapplicability of laboratory methods to field-like conditions, the inadequacy of sampling devices and other factors make determination of organic pollutants in air a challenge to the scientific community. Highly automated equipment with multiple detectors exhibiting linearity over wide concentration ranges is mandatory for rapid and dependable analytical determinations. The availability of a laboratory near the waste site, rather than setting up a laboratory on-site, is desirable since this minimizes background and cross contamination in the analytical determinations.

ACKNOWLEDGMENTS

The authors would like to acknowledge the generous support provided by the Nebraska Department of Environmental Control laboratory personnel. The projects were managed by the Superfund section of the Region VII EPA with support from the contractors: Woodward-Clyde Consultants and Tetratech, Inc. The assistance of Mr. Lee Taylor in preparation of this manuscript is also acknowledged.

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ON-SITE SOIL GAS ANALYSIS OF GASOLINE COMPONENTS USING A FIELD-DESIGNED GAS CHROMATOGRAPH-MASS SPECTROMETER

Albert Robbat, Jr. and George Xyrafas
Tufts University, Chemistry Department
Trace Analytical Measurement Laboratory
Medford, Massachusetts 02155

ABSTRACT

A Gas Chromatograph-Mass Spectrometer (GC-MS) specifically designed for hazardous waste site field investigations has been evaluated for the identification and quantification of volatile gasoline components. Response factors for benzene, toluene, ethylbenzene and isomeric xylenes have been determined. The field GC-MS responded linearly over two orders of magnitude with minimum detectable quantities of 1ppb for these compounds. The GC-MS was brought to the site for field investigation of gasoline contaminated soil. Comparative soil gas measurements are presented.

Key words: field gas chromatograph-mass spectrometer, gasoline contamination, on-site field investigation.

INTRODUCTION

The current inability of a field usable, chemical method of analysis, to unambiguously identify the wide diversity of organic compounds found on EPA's Hazardous Substance List (HSL) is increasingly becoming the critical, limiting step for hazardous waste site investigations. State and private sector environmental laboratories are overburdened with work, with data turnaround time typically exceeding several months. Clearly, an urgent need exists for analytical instrumentation capable of performing on-site chemical analysis. The obvious goal is to provide site managers with the necessary information required to make immediate decisions. A field usable gas chromatograph-mass spectrometer (GC-MS) provides the most reliable means for immediate compound identification and quantification for the diverse compounds found on the hazardous substance list. Development of reliable analytical instruments that are easily transportable and able to withstand changing climactic conditions should move the analyst from the laboratory into the field.

In another paper presented at this symposium (1), a GC-MS (Bruker Instruments) specifically designed for on-site investigations was evaluated for its ability to separate and quantify HSL volatile organic compounds (VOCs). It was found that under well-defined operating conditions the GC-MS, employing a 30m x 0.32mm i.d. fused silica capillary column with 1.8μm film of DB624, separated 31 of the 35 HSL compounds. Compounds that coeluted were differentiated based on their mass spectrum. Dynamic ranges were determined for these compounds under the same operating conditions used to separate all of the compounds simultaneously. It was found that the minimum detectable quantity was between 10 and 40 ng of compound injected (S/N=3) and that the linear dynamic range extended over two orders of magnitude.

In the present study, the applicability of field GC-MS toward VOCs will be discussed for soil gas analysis. Massachusetts Department of Environmental Quality Engineering (DEQE) allowed the authors (as part of an ongoing program, initiated in 1986) to evaluate the GC-MS for chemical analysis of a gasoline contaminated site. The gasoline vapors presently pass from groundwater through the basement floor of a church building. Initial work determined that groundwater flow is above bedrock, that the depth to bedrock is not uniform, and that the groundwater flow velocitites are low. DEQE's goal is to remove the volatile gasoline constituents from the contaminated soil beneath and around the church. The church has been closed for over a year due to the immediate health and safety risks associated with the vapors. DEQE with its contractors performed a soil gas extraction pilot study. The objective was to investigate the effect of vapor extraction from different well points; determine whether soil under the basement floor was porous (soil gas transfer); and finally, determine the effect of the water table on soil gas vapors.

EXPERIMENTAL SECTION

The experimental work reported in this paper was performed by DEQE contractors and the authors. A Foxboro century 128 organic vapor analyzer (OVA), HNU photoionization meter, and a Photovac model 10A10 GC were used by the contractors to perform their analyses. Before measurements were made by the contractors, the soil gas probes and wells were uncapped and air drawn from them to purge the dead volume. The samples were collected in an air tight syringe and analyzed by GC. Ambient air samples were collected on Tenax/Ambersorb using a low flow pump. The trapped material was analyzed after extraction by methanol using GC-MS.

A detailed description of the Brucker GC-MS and the development of well-defined operating conditions established specifically for on-site analysis of HSL VOCs under varying climatic conditions have been provided in other papers at this meeting, (Trainor and Laukien as well as Robbat and Xyrafas). The field GC-MS and the accompanying HNU (response/non-response) data were produced by the authors. Soil gas probes and wells were uncapped for two hours before VOC air sampling was performed. Samples were collected and trapped in a tube containing Tenax from the probes, wells and ambient air with a Gillian (model 513) air sampling pump. The tube was lowered about six inches into the probes and wells. The building was ventilated by opening doors and windows as allowable.

RESULTS AND DISCUSSION SECTION

Response factors, RF, were determined for the gasoline components benzene, toluene, ethylbenzene and isomeric xylenes (BTEX) as prescribed by EPA procedures. Known BTEX concentrations between the range of 10 ppb and 200 ppb and an internal standard, 1,4-difluorobenzene (50 ppb), were injected into a tube containing Tenax. The tube was placed into a GC desorption oven and held at 220 °C for 45 sec. The oven was directly interfaced to the GC-MS. The average RF percent standard deviation value for each compound based on fifteen GC-MS experiments was: benzene, 11.0%; toluene, 6.6%; ethylbenzene, 20.6%; meta plus p-xylenes, 21.0%; and o-xylene, 22.4%. A GC-MS total ion current chromatogram for the BTEX compounds at 20 ppb is shown in Figure 1. Figure 2 is representative of the typical dynamic range plots obtained using the field GC-MS for these compounds. The data presented above were obtained with the GC-MS housed in a Chevrolet Blazer, in a parking lot. Blank experiments were performed to ensure that the carrier gas, ambient air, did not contaminate the sample.

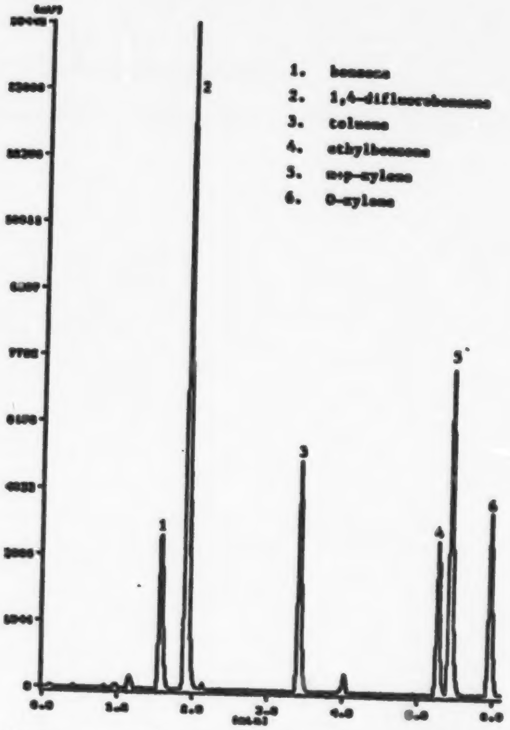

Figure 1. GC-MS chromatogram of benzene, toluene, ethylbenzene, m-,p- and O-xylene (BTEX), compounds injected onto Tenax and then thermally desorbed directly onto the GC column.

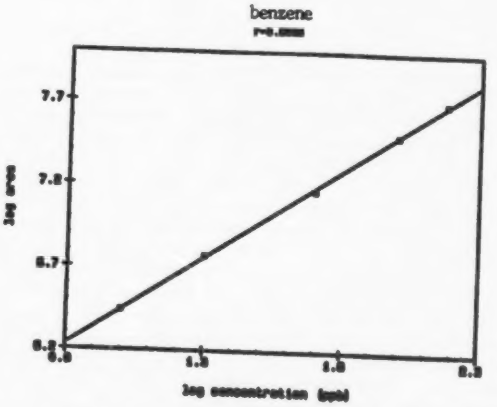

Figure 2. Linear dynamic range plot of benzene.

Figure 3 depicts soil gas probes and wells located within and around the church. Table 1 lists outside soil gas probes (J), their corresponding depths, and total BTEX concentrations. The analyses shown in the table were performed five months apart.

Since the basement floor is about five feet below the exterior ground level, the J-probes are generally at or above the floor. The HNU probe (authors) was inserted directly into the well to determine relative response before the samples were collected for GC-MS analysis. Figure 4 reveals a typical field GC-MS chromatogram. The profile is of a VOC sample collected from soil gas probe J-9. BTEX concentrations were: benzene, 13 ppb; tolune, 36 ppb; ethylbenzene, 38 ppb; m- & p-xylene, 88 ppb; and o-xylene 51 ppb. It appears from the table that the contamination is moderately localized on the southeast side. The absence of BTEX in the outside ambient air sample indicated that the sample collection procedure and GC-MS experiments were free of contamination from the site.

The height of the interior wells, I-wells, were measured from the basement floor to the water level and found to be on average 1.35 feet. The sample collection tube was placed six inches into the well. The VOC samples were collected onto Tenax tubes and thermally desorbed into the GC-MS. Figure 5 is representative of the BTEX GC-MS total ion current chromatograms obtained from the interior monitoring wells (e.g., I-2): benzene, 1.6ppm; tolune, 4.4ppm; ethylbenzene, ND; m- & p-xylene, 98ppm; and o-xylene 48.5ppm. Figure 6 is the GC-MS of the inside ambient air at the center of the basement: benzene, 60 ppb; tolune, 204 ppb; ethylbenzene, 83.5 ppb; m- & p-xylene, 444 ppb; and o-xylene 181 ppb. Table 2 summarizes the results from three separate 1988 sampling dates. As evident from the tables the GC-MS and HNU results are in excellent agreement.

The results of the soil gas study suggest that the highest concentrations of VOCs are in fact on the southeast side of the church. The highest BTEX readings were found in J-9 and 10 as well as I-1 and 2. This is the side closest to the gas station. Much lower concentrations were detected at all other wells. The apparent dramatic decrease between results of February and June may be due to the changing hydrogeologic conditions (water table), the groundwater gasoline recovery system put into operation between the respective sampling dates, and/or better vapor venting.

We have demonstrated that the field GC-MS is stable, reliable and performs under various climatic conditions (1). For example, it rained hard during the gasoline study while the RF and groundwater experiments were accomplished in 90°C temperatures and high humidity. The quality of data produced by the field GC-MS (e.g., RF, dynamic range, and field study) was shown to be statistically equivalent to commercial laboratories. The instrument provides for easy identification and accurate quantitation of the many HSL compounds normally requested of laboratory methods during comprehensive site investigations.

ACKNOWLEDGEMENT

The authors thank Bruker Instruments for use of the GC-MS instrument and Chevrolet Blazer as well as the many technical discussions related to this work. The authors also thank Jack Duggan, DEQE, for coordinating the site investigation. The authors greatly appreciate the help and interest of many other DEQE personnel for allowing us to participate in this and other environmentally important site investigations. Without their help it would have been nearly impossible to gain access to appropriate sites.

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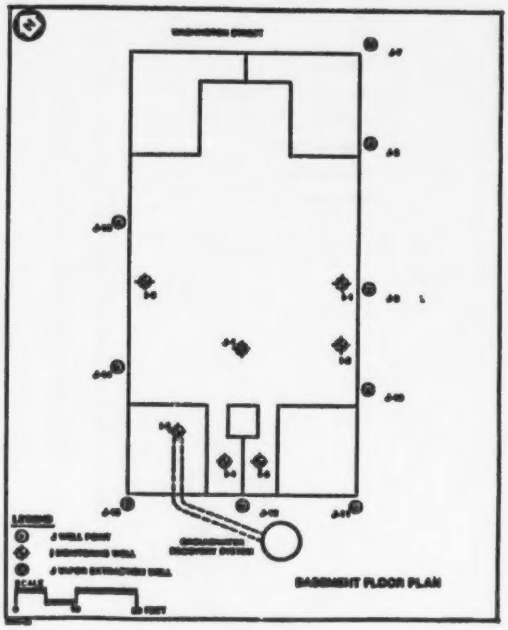

Figure 3. Interior/exterior placement of church monitoring solid gas probes and wells.

Table 1. Soil Gas Results from Probes outside of Church.

		Total BTEX Concentration (ppm)		
Location (J)	Depth(ft)	GC	GC-MS	HNU
7	9.0	ND	-	NR
8	5.0	ND	ND	NR
9	5.0	960	0.314	R
10	5.0	50	0.458	R
11	2.5	ND	ND	NR
12	5.0	ND	-	NR
13	2.5	ND	-	NR
14	4.5 refusal	ND	0.178	R
15	3.5	368.4	0.167	R
Outside Ambient Air		-	ND	NR

The GC analysis was performed on-site by a DEQE contractor, February 1 and 2, 1988.
The GC-MS analysis was performed on-site by the authors, June 29, 1988
The HNU meter was calibrated to toluene and was used to determine the relative BTEX response before samples were collected for GC-MS analysis.
- Indicates samples were not collected.

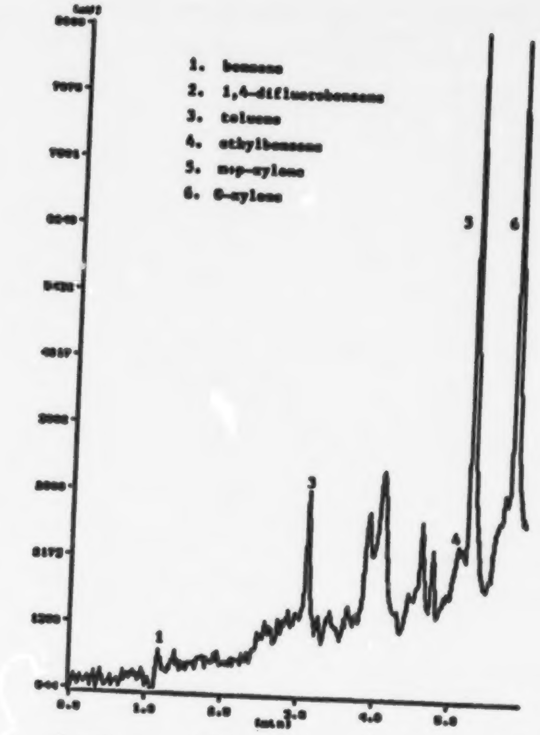

Figure 4. GC/MS of VOCs collected from J-9.

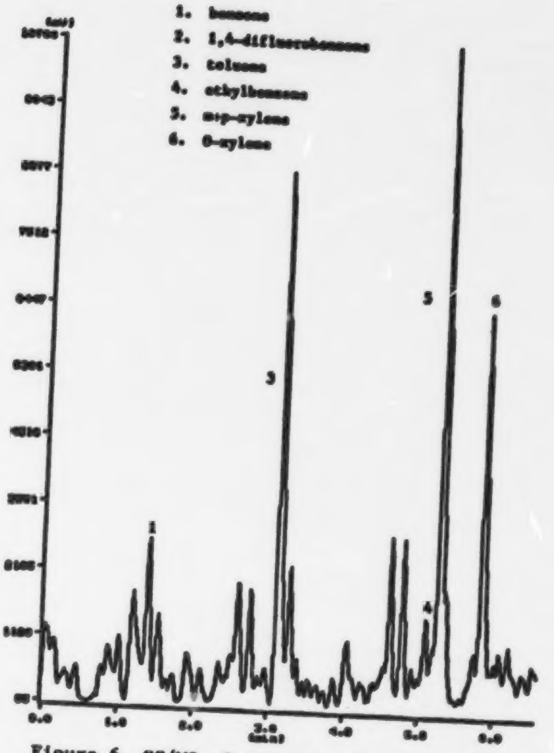

Figure 6. GC/MS of the VOC ambient air collected from within the church.

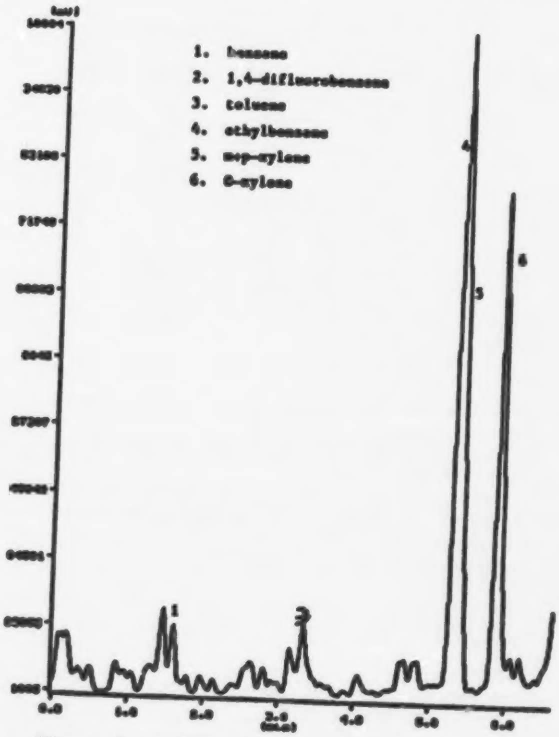

Figure 5. GC/MS of VOCs collected from (I-2).

Table 2. Soil Gas Results from Interior of Church

	Total BTEX Concentration (ppm)		
Location	GC	HNU	GC-MS
I-1	16,271	160	199.9
I-2	9,641	155	152.5
I-3	1,217	4	0.4
I-4	440	12	0.3
I-5	27.4	30	-
I-6	44	20	16.7
SUMP	-	2	1.6
J-1	-	-	5.1
Inside Ambient Air	2.4	1.0	1.0

GC analysis performed on-site by DEQE contractors, February 1 and 2, 1988.
HNU analysis performed by DEQE contractors April 7, 1988.
GC-MS analysis performed on-site by authors, June 29, 1988
All analytical instruments calibrated for benzene, toluene, ethylbenzene and isomeric xylenes.
- Indicates samples were not collected.

REFLECTANCE SPECTROSCOPY (0.2 to 20 μm) AS AN ANALYTICAL METHOD FOR THE DETECTION OF ORGANICS ON SOILS

Trude V.V. King and Roger N. Clark, U.S. Geological Survey,
P.O. Box 25046 MS 964, Denver, Colorado, 80225, USA

ABSTRACT

Reflectance and transmission spectroscopy (2 to 20μm) has been used as method for the identification of organic solvents on a soil. Fundamental C-H stretch absorptions (~3.4μm) and the overtones of these absorptions, which occur at ~1.7μm, can be used to uniquely characterize the organic solvents. Spectral differences exist between toluene, benzene, trichloroethylene and gasoline in transmission spectra and in reflectance spectra when they are mixed with a Na-rich clay. Key words: reflectance spectroscopy; organic solvents; transmission spectroscopy.

INTRODUCTION

Reflectance spectroscopy is a quick and inexpensive method for identifying organic contaminants in both surface and sub-surface environments, for example:

1. Mapping the aerial distribution of potentially hazardous spills.
2. Identifying the potential sources of hazardous and/or toxic materials.
3. Monitoring toxic sources as a function of time, e.g., during and after a water rejuvenation program.

Laboratory experiments using mixtures of clay standards and organic contaminants have shown that it is possible to identify both the clay and the associated organic contaminant by reflectance spectroscopy methods. Samples of neat clays and organic solvents have been measured in both transmission and reflectance modes (0.2-20 μm) to characterize fundamental and overtone vibrational absorptions as well as crystal field absorptions. These spectra are entered in the U.S.G.S reference sample data base and used as comparison standards for unknown mixtures. Attempts are underway to estimate abundances of organics in a clay mixture using a radiative transfer model by deriving absorption coefficients and index of refraction for the materials of interest. These techniques could help evaluate environmental problems by in-situ measurements, laboratory measurements, and potentially with airborne imaging spectrometers.

DISCUSSION

Most minerals, organic and chlorinated solvents show diagnostic absorption features in the reflected solar radiation part of the spectrum (0.3 to 2.5μm) and in the infrared part of the spectrum (3 to 200 μm). These absorption features can be used to determine the mineralogy of the surface, and in a number of cases, the trace elements present in those materials. In addition, spectroscopy can identify organic and chlorinated solvents which may be associated with a specific mineral or mineral assemblage.

Laboratory calibration investigations included clay/organic mixtures in which the organic phases were characterized by transmission measurements and then mixed with a host-clay and characterized by reflectance measurements. Transmission spectra of benzene, methanol, toluene, trichloroethylene, and gasoline show numerous absorptions in the near infrared (Figure 1). These absorptions are different in position and shape from mineral and water absorptions, making their detection easy. Because the intensity of absorption bands vary with wavelength (i.e. fundamental absorptions are stronger than overtones) detectability levels are a function of the absorption feature selected for analysis. Thus, detectability limits can range from parts-per-million (ppm) to a few percent.

Simulations of likely environmental problems involved mixing the solvents with montmorillonite. There was no additional sample preparation and spectral measurements took less than fifty minutes per sample. Spectrometers with detector arrays could reduce the measurement time to less than one second. Figure 2 shows the near-infrared reflectance spectra for the neat Na-montmorillonite sample (SWy-1) and the mixtures of montmorillonite and solvents. In each example the clay was mixed with large quantities of the solvent for illustrative purposes, however detection levels in this spectral region are on the order of 1 wt%, when computer analysis is employed. In samples of montmorillonite mixed with gasoline, gasoline bands are prominent between 1.65-1.8 μm, and near 2.3 μm. The benzene bands are very strong in the 1.7, 2.16 and 2.46 μm regions when mixed with montmorillonite at the 33 and 14 wt% levels. The toluene absorptions are very strong, at 1.15, 1.68-1.7, 2.2, and

2.35-2.45 μm, in mixtures of 28, 14 and 7 wt.%. The absorptions from trichloroethylene are very strong in the montmorillonite at 24 and 39 wt.%.

The absorptions in the 1-2.6 μm region are combination overtones. The fundamentals, some of which occur in the 3-5μm region, are 30 to 100 times more intense.

Figure 3 shows the mid-infrared spectra of gasoline (super-unleaded), measured in transmission mode, and the reflectance spectra of montmorillonite (SWy-1) and mixtures of montmorillonite and gasoline. The prominent C-H stretch vibration between approximately 3000-2800 cm^{-1} wavenumber (~3.33-3.5 μm) is used, in this example, to illustrate the capabilities of spectroscopy in the detection and identification of organic/clay mixtures. As the amount of organic contaminant decreases the strength of the fundamental band also decreases. However, based on these measurements in the 3.3-3.5-μm wavelength region, detection limits might be as low as 10 to 30 ppm.

APPLICATION

Mapping the aerial distribution of potentially hazardous spills using airborne reflectance spectroscopy techniques will require a timely response and instrumentation with high spectral resolution and signal to noise. Slow rates of penetration of the organic material into the underlying soil should in most instances, hold the organic for a period of time sufficient for remote detection. However in some instances, a quick response to assess spills would be necessary before the organic material evaporates. Advantages of mapping the aerial extent of a spill using airborne remote spill as well as providing a synoptic view which is difficult too obtain by ground-based observations.

In-situ methods of spectral characterization can use the remote, airborne-type of spectroscopic study mentioned above either independently or in conjunction with laboratory measurements. Laboratory measurements, similar to the results presented in Figures 1-3, of samples collected from specific sites could aid in determining the direction of movement of a toxic plume. By collecting samples in the field and returning them to the laboratory in sealed sample holders, the integrity of the sample would not be compromised. Laboratory measurements using currently available technology can more accurately determine low concentrations of organic contaminants in soils than instruments now available for synoptic field measurements because of greater spectral resolution. Maps of the concentrations of organic contaminants in soils would provide information on the source (type of organic or chlorinated solvent) and the direction of movement. An added benefit of the spectroscopic method of mapping organic/solid interactions, is the possibility of detecting and characterizing secondary changes in the contaminant as a result of chemical or physical reactions with the surrounding material.

Down-hole spectroscopic measurements would prove beneficial for the characterization and monitoring of organic/solid interactions below the Earth's surface. Although instrumentation does not currently exist for these types of measurements, infrared fiber optics could be used. Down-hole spectroscopy will provide in-situ measurements for non-recoverable, subsurface samples. This method of measurement would be valuable for monitoring the concentration of organics contaminants in soils as a function of water rejuvenation. Because much of any spill is caught and held by the soil, it would be beneficial to monitor the changes in organic contaminant concentrations as a function of time.

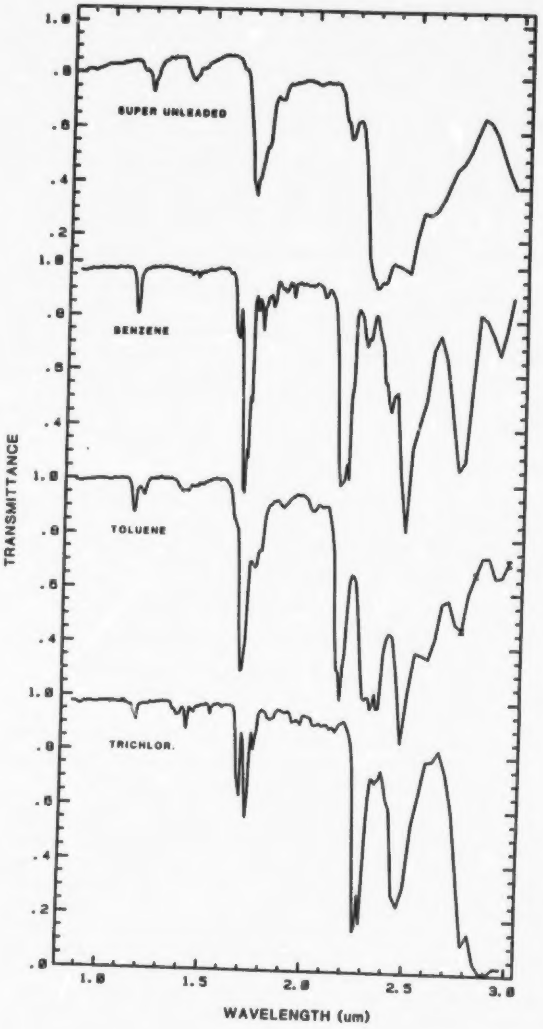

Figure 1. Transmittance spectra (0.1mm thick) of super unleaded gasoline,benzene, toluene,and trichloroethylene in the 0.9-3.0-μm wavelength region show the characteristic overtone and combinations features of the solvents. Of particular interest is the 1.7-μm wavelength region whih is the first overtone of the fundamental C-H stretch which occurs near 3.4μm.

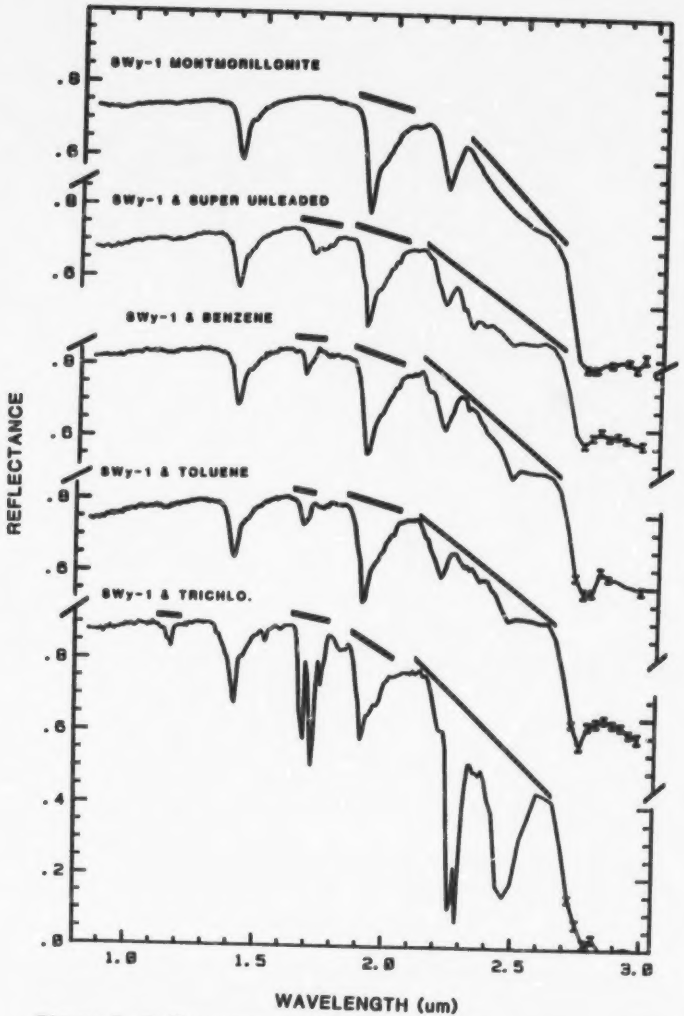

Figure 2. Reflectance spectra of SWy-1 (Na-montmorillonite) and SWy-1 mixed with super unleaded gasoline, benzene, toluene and trichloroethylene. In the mixed spectra, it is possible to identify spectral characteristics of the clay and the mixed contaminant. Although all the mixed spectra have adsorptions at similar wavelength positions(eg. 1.7μm), absorptions features related to contaminants can be distinguished from one another based on exact position and intensity. Absorption features which are correlated, to some degree, with the presence of organics in the clay are marked with bars.

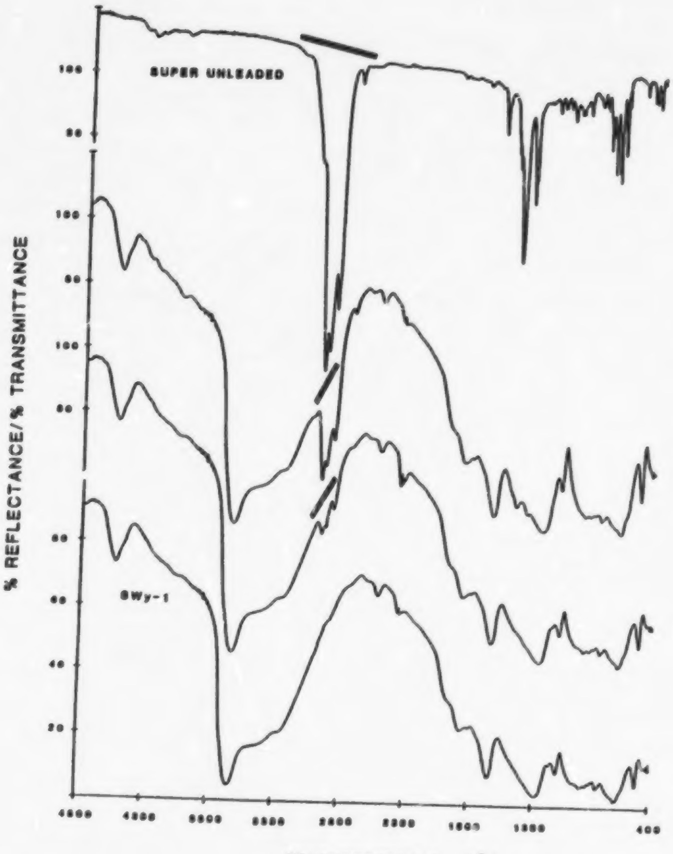

Figure 3. Transmittance spectra of super-unleaded gasoline (top spectra) shows the vibrational absorptions of gasoline from 2 to 25 μm. The strongest adsorptions in the 3.6-μm wavelength region is attributed to the C-H stretch in the gasoline (shown by bar). The bottom spectra is the reflectance spectra of SWy-1 (Na-montmorillonite) without added gasoline and shows the OH-absorption region (~2.7μm) characteristic of the clay. The two intermediate spectra illustrate the mixture of ~12 wt% and 1 wt% gasoline in the clay. The fundamental C-H adsorption is detectables in both intermediate spectra and illustrates the usefulness of reflectance spectroscopy in identifying clay/organic mixtures.

FIELD USE OF A MICROCHIP GAS CHROMATOGRAPH

R.W. Sherman, T.H. McKinney, Institute for Environmental Studies, LSU, Baton Rouge, LA,
M.F. Solecki, National Oceanic and Atmospheric Administration, Seattle, WA
R.B. Gaines, U.S. Coast Guard R&D Center, Groton, CT
B. Shipley, U.S. EPA Region 9, San Francisco, CA

When responding to chemical emergencies and evaluating waste sites it is important to have accurate information about the identities and quantities of the chemicals involved. It is advantageous to have real time information so that response personnel and project managers may make timely decisions to accelerate mitigative actions, cleanup, and to adequately protect workers and the public.

A field deployable microchip gas chromatograph linked to an external personal computer has been used to evaluate the nature and extent of contamination at a number of hazardous waste sites and chemical emergencies. The system has been used to analyze air and water samples as well as identify the contents of drums containing volatile liquids.

The instrument used for these field deployable analyses was a Michromonitor500 (Microsensor Technologies, Inc., Fremont, CA) interfaced with a Macintosh personal computer (Apple Computers, Cupertino, CA). The Michromonitor500 (M500) contains four high resolution microchip gas chromatographs (µGC) with capillary columns and thermal conductivity detectors. Vapor samples are introduced with an internal vacuum pump, and the sample is routed to the appropriate µGC. Each µGC has a different length capillary column and is used to analyze volatile compounds with a predefined range of volatility. The M500 is designed to be portable and has the ability to identify several dozen compounds which have data stored in its internal ROM library (1). The device as it comes from the manufacturer will detect only those vapors which were preselected. Other compounds could be present but would go undetected if data are not contained in the library. This limitation is overcome by the use of user-friendly software which has been developed to run on a Macintosh computer. The connection between the M500 and the Macintosh may be a direct link with wires, telephone lines, radio frequency modems, or any combination of these.

The Macintosh software contains three modes of operation. The first mode allows access to all of the M500's standard features by having the Macintosh emulate the control panel of the M500. This mode is particularly useful for troubleshooting and debugging.

The second mode of operation has the M500 dump raw digital data to the Macintosh which converts the data into high resolution gas chromatograms. This allows an evaluation of peak shapes, elution profiles, and instrumental parameters such as drift.

The third mode of operation is the most complex, but it provides more useful anlytical data. The M500 analyzes a sample and stores the temperature, data on the retention times, and peak areas for all peaks in the chromatogram. These data are transmitted to the Macintosh. The Macintosh uses the temperature and the retention time of the air peak to calculate expected retention times for normal hydrocarbon standards as if they had been analyzed with the sample. Using these calculated hydrocarbon retention times the software then calculates modified Kovats retention indices for all peaks in the chromatogram (2). Identification is made by comparison of the retention index of the unkown compound with library values which are a part of the Macintosh software.

Since the M500 has a small sample loop and uses a thermal conductivity detector, the detection limits for most compounds are about 10ppm. Since this detection limit is too high for most environmental applications, a sample preconcentrator has been developed to lower detection limits by factors of 100 (3). This device is used to concentrate large samples of volatile organic compounds (200-500 mL) on ambient temperature sorption traps and desorb the organics at 250°C into smaller volumes (2 mL). The traps use a combination of Tenax GC and Spherocarb as the sorbents. In addition to concentrating air samples this device may be used to concentrate volatile compounds from water samples using a purge and trap technique.

This analytical system has been used at a number of waste sites, emergency removals, and fires involving hazardous materials. It has been used by LSU personnel, Members of the Coast Guard Atlantic Strike Team, and Pacific Strike Team, EPA Region 9, and the EPA-Environmental Response Team. Brief descriptions of some of these field uses are given below.

In April 1986 the M500-Macintosh system was used to analyze drums at a Superfund site in Utah. By using the M500 and a HAZCATT procedure the drums were prepared for disposal with a reduced need for laboratory analysis.

In November 1986 the system was used to sample the contents of underground storage tanks at an abandoned latex manufacturing plant in New Jersey. The results given by the M500 in real time were consistent with the results of GCMS analyses which were performed off site and had a turnaround time of several days.

In February 1987 the system was used at a chemical storage facility in Maryland. The M500 was used to verify that drums were labelled correctly. It was not necessary to send samples for laboratory analyses, and an estimated $50,000 was saved.

In the spring of 1987 the M500 was used at a fire located at a rubber manufacuring facility in Virginia. Some firefighters were using the runoff water to wash themselves and their clothing. The M500 detected benzene, toluene, and other hydrocarbons in the headspace of the runoff water. The operator of the M500 informed the fire chief, and recommended that the fireman stop rinsing in the runoff, and any firemen who had been in the runoff water go to the hospital for observation. In the ambulance on the way to the hospital several firemen broke out with a rash.

In August 1987 the M500 with a concentrator was used at a Superfund site in Washington. Although primarily used for air monitoring, the M500 was also able to identify contents of unlabelled drums which were uncovered during the excavation process.

In the fall of 1987 the M500 was used at a drum removal action in California. The M500 yielded data which was consistent with labels and HAZCATT information. The drums were able to be disposed of with no further analysis, resulting in a considerable savings.

In winter of 1987 the M500 was used for air monitoring at two municpal landfill fires in Hawaii. The M500 was used along with other field instruments, including another field GC. The M500's results were consistent with all of the other instruments, but it provided data much quicker and was found to be easier to set up and maintain.

The previous examples, and others, have demonstrated the value and usefulness of these high resolution field deployable analytical devices for a wide variety of field applications.

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RAPID ASSESSMENT OF PCB CONTAMINATION AT FIELD SITES USING A SPECIALIZED SAMPLING, ANALYSIS AND DATA REVIEW PROCEDURE

William W. Freeman
Principal Scientist
Roy F. Weston, Inc.
West Chester, PA

Joel Karmazyn
Senior Project Scientist
Roy F. Weston, Inc.
West Chester, PA

ABSTRACT

An operational procedure was needed to accurately assess the extent of PCB contamination at field locations in as short a time and as economically as possible. The procedure which was developed includes a sampling grid lay-out and expansion scheme, a rapid extraction/analysis procedure and a data validation step. Most results are "turned around", including the grid expansion-decision making process in 48 hours. Key factors include the rapid extraction procedure and the use of a laboratory dedicated to the analysis of just these samples.

The objective was not only to obtain accurate test results in a timely manner, but also to make efficient, economical use of the field team's time. The entire "turn-around" process is described here, from the original identification of potential PCB sources at the site, through sampling procedures, transfer to the dedicated lab, analytical procedures and data review.

When site assessment begins, a standard sampling grid pattern is used. Grid expansion procedures are described in which each PCB detection point will generate 2 to 4 new sampling points, depending on their location in the grids. After reviewing and validating the lab data on a daily basis, a decision is made whether to extend the grids, stop sampling in a particular direction, resample specific areas, etc.

While evaluating analytical procedures, several proven and accepted extraction/analysis techniques were examined before choosing an orbital shaker extraction method and gas chromatography technique which would provide the best combination of speed and accuracy. The procedure is described wherein 10 gram samples of soil are extracted for 30 minutes and then tested for PCB content. Standard QC and QA procedures are employed, including field blanks, matrix spikes, duplicate samples, etc. This procedure can be used for specific action levels such as 10 or 25 ppm etc., as well as general site characterization.

Sample transport time, analysis, and data review are all coordinated between the field team and home office so that no time is lost. For example, while waiting for analytical data from a particular on-site grid area, the field team can be sampling other on-site or off-site areas, extending grids from areas previously found contaminated, etc. One of the chief advantages of this sampling and analysis procedure is that it facilitates the rapid characterization of plumes of surface contamination.

INTRODUCTION

Once a site of known or potential PCB contamination has been identified at a field location, it is desirable to obtain analytical results for soil samples as soon as possible. This aids in making preliminary decisions regarding the extent of contamination and the type of remedial action which may be required. Project management personnel need information fast in order to make decisions on depths for soil borings, directions of sampling grids, etc.

A procedure was developed which not only enables project personnel to obtain accurate test results in a timely manner, but also makes economical, efficient use of the field teams' time.

The effectiveness of this procedure is based on the coordination of many aspects of the operation. These include the sampling team, the delivery personnel (sample "runners"), laboratory receipt custodians, lab analysts and the data review personnel. A laboratory with personnel and equipment dedicated to the analysis of just these samples is used.

When properly coordinated, this unique operational procedure allows the field team sufficient time to sample other areas of interest while waiting for results from previous samples. Management can quickly acquire and assess the results and relay instructions on items such as grid expansions to the field team. The entire procedure, including the decision making process, can be accomplished within 48 hours (or less) from the time that a set of samples is taken at the field site.

Procedures such as pre-labeling bottles, pre-printing Chain-of-Custody forms and the use of a dedicated delivery person to transport samples between the site and the laboratory help in the rapid and efficient assessment of the extent of the PCB contamination.

PROCEDURE SUMMARY

Once the potentially contaminated area has been identified and the field sampling team with it's equipment is set up at the site, the following general sequence of events takes place.

1. Survey site; lay out initial sampling grids.
2. Take initial sets of samples.
3. Preserve and package samples for same day or overnight delivery to the laboratory.
4. Laboratory personnel perform rapid extraction procedure and gas chromatography analysis at the laboratory dedicated to the analysis of just these samples.
5. Field personnel continue sampling activities in other areas while waiting for initial test results.
6. Data review personnel perform validation and "reasonableness" checks on lab data.
7. As validated test results become available (usually within 48 hours), project management personnel make decisions regarding grid expansions or other additional sampling procedures.
8. This sequence should continue until the site assessment procedure is complete.

SPECIFIC PROCEDURES

1. Soil Sampling Grids

The soil sampling grid system should be established by surveying selected sampling locations, using fixed objects s reference points if possible. Other sampling location/grid nodes should be surveyed so that the overall grid system is well defined. Survey stakes should be set up at the four corner grid locations that surround a potential source of contamination and then a standard 25-foot square grid system should be put in place.

Once the grid has been established, surface soil samples should be collected from each corner of the 25-foot square and (optional) a composite sample from within the square, approximated by the center of the square.

2. Sampling Activities

Standard sampling equipment and procedures should be used. The equipment includes stainless steel augers, scoops and trowels, mixing bowls for homogenizing composites, etc. Clean sample containers of the proper size and composition should be used. Pins or wire/plastic flags should mark all sample locations.

The actual sampling procedure, including type, number and depth of samples should be delineated on a site specific basis. All QC samples such as duplicates, blanks, etc., should be included in the sampling plan and strictly adhered to by the field personnel.

3. Packaging/Shipment of Samples

This is one of the more important phases of the rapid turn-around site assessment procedure. It is crucial that samples are identified, packaged, preserved and shipped to the dedicated laboratory in the proper fashion. Complete identification information must be recorded on the sample container label as well as on the Chain-of-Custody sheets (see example in Figure #4), including exact location of the sample as well as the tests that are to be performed at the laboratory.

All standard practices involving sample integrity, safety, D.O.T. regulations, etc., should be followed. These include items such as custody seals on jars, placing ice in the shipping container for sample preservation and using the correct labels for shipping any hazardous (PCB) materials.

In order to insure that the samples arrive at the dedicated lab as soon as possible, a "runner" should be utilized whenever possible both to deliver samples to the lab and bring new materials to the field site. This procedure, using a dedicated van and driver, is practical and efficient even if the field site is up to 100 miles from the lab. It enables samples to be delivered to the laboratory on the same day that they are taken, so that the analytical process can begin as soon as possible. At least one round trip per day can be made and possibly more, depending on the distance involved.

In lieu of a dedicated "runner", an overnight delivery service can be utilized. This is not as efficient as a dedicated driver and van, but will get the samples to the lab late on the morning following the sampling events of the previous day.

4. Continuation of Sampling Activities

While waiting (up to 48 hours) for results on a particular set of field samples, other activities such as additional surface soil sampling, soil borings, groundwater or surface water sampling, etc., can be carried out. If these types of events are scheduled at least 2 days in advance, then continuous, efficient use can be made of field personnel and sampling teams.

5. Data Review

When results become available from the dedicated laboratory, they should immediately be delivered to the project personnel who perform the data review process. This review of the "quick-turn-around" data cannot be as complete as, for example, the validation of a complete Tier II data package. However, since the data will be used for grid expansions and other field related activities, it is important to have a review step in place.

The review should include items such as matching the Chain-of-Custody sample IDs with the data summary IDs, checking dilution factors, reviewing QC data (e.g. matrix spike/matrix spike duplicate), etc. If discrepancies are discovered, a more detailed review of the lab data including the chromatograms can be conducted.

This review step should also include a "reasonableness" check by someone familiar with the specific site and the sampling locations. This check is as important as the analytical data review even though it is only a quick check of test results-vs-sample locations. Since field sites may often yield dozens of samples, depending on grid expansions, it is necessary to perform this "reasonableness" check in order to help assure that test results reflect the true location of PCB contamination areas.

The analytical review and "reasonableness" check should take no more than one hour even for a batch of up to 20 samples. It is convenient to use a checklist such as the one shown in Figure #5.

6. Decision Making

As soon as validated test results become available, they should be delivered simultaneously to the site supervisor and the project manager. "Delivered" means at least by telephone and preferably in hard copy form. This can be accomplished by use of a telefax machine in a mobile office at the site or, when practical, delivery of reports to the site by the dedicated runner during a trip to the site.

The data should then be examined by the site supervisor and project manager and decisions made as soon as possible regarding grid expansions. Site maps or prints should be available at both the home office and field site to aid in identifying exact field locations.

This sequence of sampling - analysis - decision making - grid expansion - sampling, etc., should be continued until the sampling plan is completed or terminated due to grid overlap.

7. Material Preparation

In a site assessment/sampling operation, one of the most time consuming activities involves the filling out of documents such as Chain-of-Custody forms and properly identifying the numerous sample containers. A key to conducting a rapid, efficient, economical operation such as this is the use of pre-printed Chain-of-Custody forms (see sample, Figure #2) and pre-labeled sample jars.

Once the initial sampling grids are defined, forms can be pre-printed and jar labels filled out for these locations. Any minor variations in the sampling scheme can simply be crossed off or corrected on the forms, as necessary. As analytical data is received from the lab, validated, and grid extension decisions are made, the next batch of Chain-of-Custody forms and jar labels can be prepared. The dedicated runner can also assist in bringing forms and labeled jars from the home office.

THE DEDICATED LABORATORY

During this type of remedial investigation or site assessment, one of the most expedient ways to generate rapid, accurate analytical data is to make use of a "dedicated laboratory". This type of facility can typically analyze twenty (20) or more soil or sediment samples per day for PCB content, and provide results in approximately forty-eight (48) hours, or less, from the time the samples are taken.

1. Analytical Procedures

Analyses of PCBs for screening purposes can be conducted at prescribed characterization levels such as 5, 10, or

25 ppm in soil samples. The laboratory can use a rapid extraction technique[1] similar to the one developed by the U.S. EPA Releases Control Branch. Other extraction procedures including the soxhlet method were evaluated at the WESTON Analytics Laboratory in Lionville, PA, but the referenced rapid extraction procedure provided the best combination of speed, low cost and accuracy at characterization levels of as low as 5 ppm for PCBs in soil. The chosen procedure can include an acid clean-up of the extract and analysis by gas chromatography.

2. Method Summary

Ten (10.0) grams of sample is placed in a 250 ml screw top Erlenmeyer flask or glass jar. Eighty (80) ml of hexane and twenty (20) ml of methanol is added directly to the flask or jar. The container is placed on a gyrotory shaker unit positioned behind a safety shield in a fume hood and then is shaken at 400 rpm for thirty (30) minutes. The flask is then removed to a stationary area, where the suspended solids and particulate matter is allowed to settle for approximately thirty (30) minutes.

The hexane extract is removed using Pasteur pipets while avoiding agitation of the soil/sediment layer or particulates in the bottom of the flask. The sulfuric acid clean-up is performed at this point. The analysis for PCB content is then conducted by electron capture gas chromatography under conditions similar to those shown in Appendix A.

A separate test for percent moisture (drying at 105°C) can be run concurrently. Results (PCB content) should be expressed on a dry weight basis.

3. Quality Assurance & Quality Control Checks

The daily quality of the analytical data generated by the dedicated laboratory is monitored by the analysis of method blanks, fortified method blanks, etc. External (field) quality control samples typically include field and trip blanks and field duplicates.

The purpose, description and frequency of laboratory QC samples typically used in the dedicated laboratory facility at the WESTON Analytics Laboratory are shown in Appendix B.

Quality Control samples should represent a minimum of 5% of the field samples. Fortified samples are spiked at WESTON Analytics with a commercially available Aroclor 1254 PCB standard. The blank matrix consists of a 10 gram sample of sodium sulfate. Table I represents a typical statistical evaluation of lab QA data. The average percent recovery for matrix spikes and matrix spike duplicates was 100.5%. As an additional QA step, and to help confirm the accuracy of the rapid extraction method, approximately 10% of the samples can also be analyzed for PCBs using more conventional methods. WESTON Analytics routinely performs this type of program for PCB contaminated soils. A very good correlation has been obtained using both the rapid extraction method and the SW-846 method. A comparison of typical PCB analysis results obtained by both methods is shown in Table II.

SUMMARY

Site assessment sampling activities for known or potentially contaminated soils and sediments can be conducted in a rapid, efficient and accurate manner if all aspects of the operation are coordinated properly. The time (and dollars) spent by having a sampling team and mobile equipment in the field can be minimized by use of:

- o A field team that has pre-planned their activities.
- o A rapid delivery system (dedicated "runner") for samples and materials.
- o The use of pre-planned paperwork and sample containers.
- o A dedicated laboratory for 48-hour (or less) turnaround of analytical results.
- o Coordination between the field supervisors and project management personnel regarding data review and decision making.

The major advantage of this type of program is the ability to make timely decisions regarding items such as the direction of a contamination plume, construction and extension of sampling grids and managing the field team's time. If the sample delivery system, dedicated laboratory and decision making process all function as designed, the field team should have no "down" time until they are waiting for what is presumed to be the last batch of lab results. Even then, the time can be used for activities such as decontamination of equipment, updating maps, etc., while waiting for the "final" set of analytical data.

REFERENCES

[1] Emergency Response Analytical Methods for Use On Board Mobile Laboratories. Draft Document, June 1987.

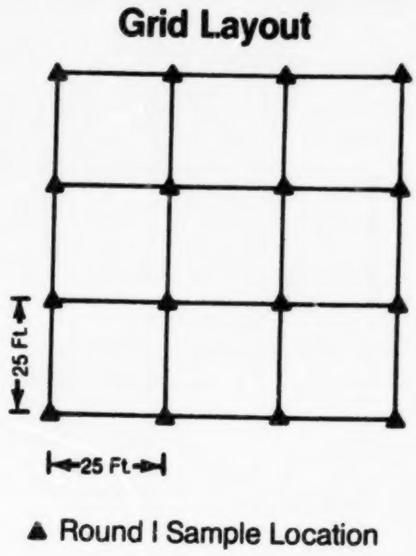

Grid Layout
25 Ft
25 Ft
▲ Round I Sample Location

FIGURE #1

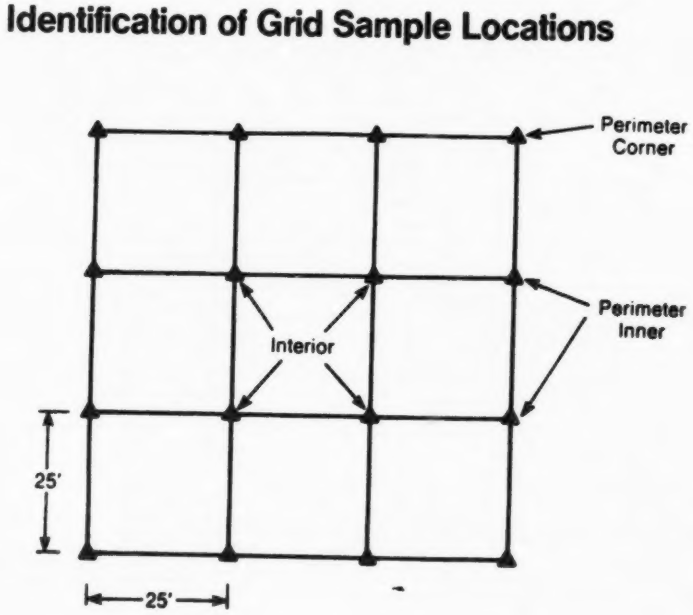

Identification of Grid Sample Locations
Perimeter Corner
Perimeter Inner
Interior
25'
25'

FIGURE #2

Expansion of Grid Based on Round 1 Test Results

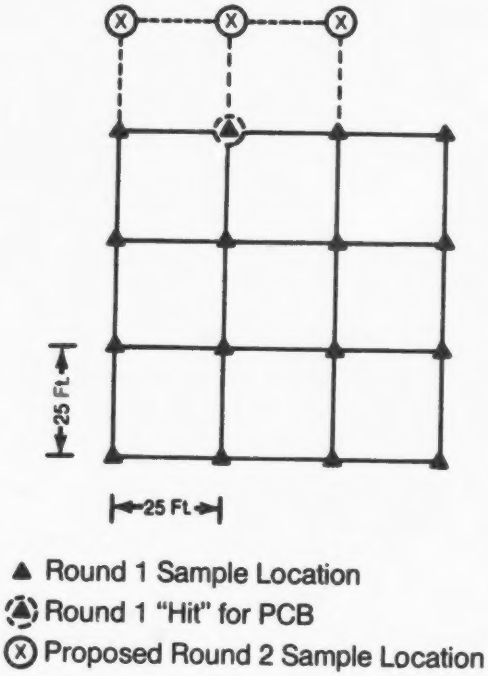
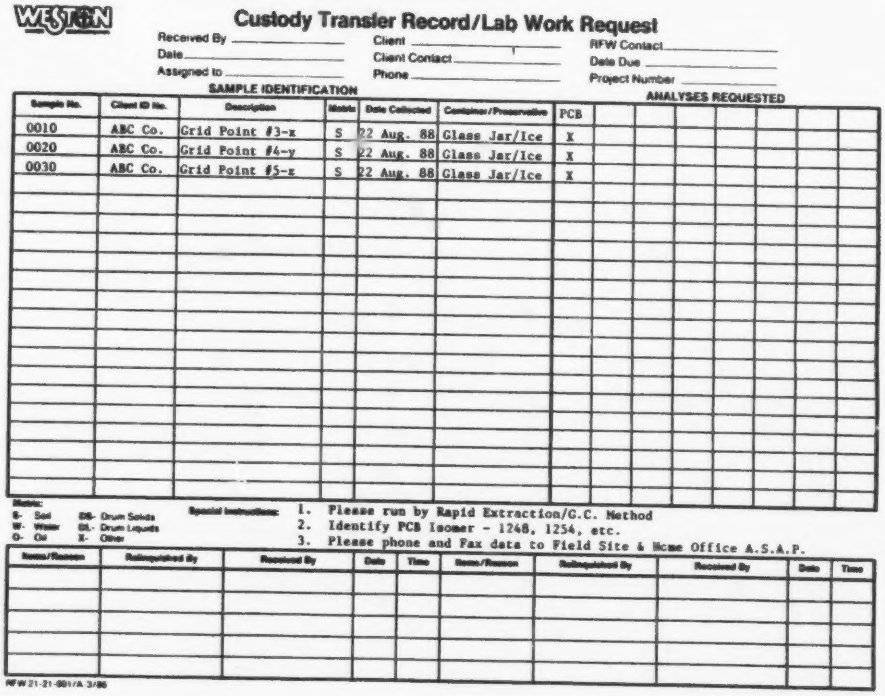


FIGURE #3



WESTON

Custody Transfer Record/Lab Work Request

Received By ______ Client ______ RFW Contact ______
Date ______ Client Contact ______ Date Due ______
Assigned to ______ Phone ______ Project Number ______

SAMPLE IDENTIFICATION — ANALYSES REQUESTED

Sample No.	Client ID No.	Description	Matrix	Date Collected	Container/Preservative	PCB							
0010	ABC Co.	Grid Point #3-x	S	22 Aug. 88	Glass Jar/Ice	X							
0020	ABC Co.	Grid Point #4-y	S	22 Aug. 88	Glass Jar/Ice	X							
0030	ABC Co.	Grid Point #5-z	S	22 Aug. 88	Glass Jar/Ice	X							

Matrix:
S- Soil DS- Drum Solids
W- Water DL- Drum Liquids
O- Oil X- Other

Special Instructions:
1. Please run by Rapid Extraction/G.C. Method
2. Identify PCB Isomer - 1248, 1254, etc.
3. Please phone and Fax data to Field Site & Home Office A.S.A.P.

Items/Reason	Relinquished By	Received By	Date	Time	Items/Reason	Relinquished By	Received By	Date	Time

RFW 21-21-001/A 3/86

FIGURE #4

DATA REVIEW CHECKLIST

Site Name:____________ **Delivery Due Date:**___________ **Reviewer:**_______________

Batch ID #____________ **Date:**___________________

Task	Yes	No	NA	Comments
Chain of Custody Matches Sample IDs				
Sample Holding Times Met *				
Case Narrative Flagged Samples Exceeding Holding Time *				
Data Summary Sheet Matches Chronology				
QC Data Included				
Matrix Blanks Clean				
Matrix Spike Recovery Acceptable				
Appropriate Detection Limits				
J - Values Correct/Missing				
B - Values Correct/Missing				
U - Values Correct/Missing				
MS and MSD Recoveries Reported In Percentage				
Case Narrative Describes Analytical Difficulties *				
Typos				

*Where applicable

Other Comments/Reasonableness Check:

Date Submitted To Project Manager:___________

Submitted For Revisions:_______________ **Response Due Date** ___________

Returned To Reviewer:_______

Date Of Package Approval:________

Initials:________________________

____

FIGURE #5

TABLE I

STATISTICAL EVALUATION OF TYPICAL QA DATA

QC Parameter	No. of Samples	Results
Matrix spike, matrix spike duplicate	40	Avg. % Recovery = 101% (Std. Dev. = 16.5)
Blank spike/blank spike duplicate	25	Avg. % Recovery = 103% (Std. Dev. = 12.9)
Duplicate samples	40	Relative % Difference = 24%

NOTE: The relative percent difference (RPD) is a measure of the analytical precision of the laboratory procedure. The Contract Laboratory Program has established a guideline of 50 or less RPD for the analysis of PCBs in soil The RPD of 24 for this rapid extraction method is well within the guideline.

TABLE II

Comparison of Analytical Results for Samples Extracted by the Rapid Extraction Method and EPA SW - 846 Method

Sample No.	PCB Content (mg/kg)	
	Rapid Extraction	SW-846
1	3.0	2.5 J
2	2.1	5.3
3	23	27 J
4	27	13
5	220	37
6	.61 J	.66 J
7	.56 J	1.8 J
8	36	22
9	6.8	273
10	ND	3.5 J
11	2.3	2.0 J
12	3.4	2.8
13	18	17
14	4.0	110
15	5.0	7.7
16	120	120
17	14	9.3
18	ND	.17 J
19	17	12
20	1400	980

NOTES:

ND - Not Detected
J - Present below detection limit

APPENDIX A

TYPICAL GAS CHROMATOGRAPHIC CONDITIONS

Analytical Columnm: *	1.5% SP 2250/1.95% SP 2401 on 100/120 Supelcoport 6 ft x 4 mm glass column (mixed phase support)
Carrier Gas:	Argon:Methane (95%:5%)
Carrier Flow Rate:	40 ml/min
Detector:	Electron Capture (ECD)
Detector Temperature:	260°C
Injector Temperature:	225°C
Oven Temperature:	180°C (Dependent on PCB Aroclor)
Program Rate:	Isothermal
Time of Analysis:	Variable (Dependent on PCB Aroclor)

* The mixed phase column recommended for PCB analyses should be packed and conditioned in accordance with Method 7.3 (Instructions for Packing and Conditioning Glass Analytical Columns for Gas Chromatography Instruments) and performance tested according to the procedure and specifications described in Appendix C of Method 7.4 (Protocol for Performance Testing Packed, Conditioned, Glass Analytical Columns for Gas Chromatography Instruments).

APPENDIX B

Purpose and Frequency of Laboratory Quality Control Samples

(Typical for PCB in Soil Analyses)

Sample Type	Purpose	Frequency
Method Blank	Monitor Laboratory Contamination	Daily with each preparation batch of 20 or fewer samples
Fortified Method Blank	Laboratory Accuracy	Daily with each preparation batch of 20 or fewer samples
Field Blank	Monitor Sample Collection	Daily or once for each sample collection method
Trip Blank	Monitor Contamination during Field Operations	At least once per sampling episode
Fortified Sample	Monitor Bias due to Sample Matrix	As required by analytical protocol per batch of 20 or fewer samples
Duplicate Sample	Monitor Precision	As required by analytical protocol per batch of 20 or fewer samples

First International Symposium
Field Screening Methods for Hazardous Waste Site Investigations
Participants' List

Prabha Acharya
Arizona State Laboratory
1520 W. Adams
Phoenix, AZ 85007
(602) 255-1188

James H. Adams, Jr.
USEPA, Region V
536 South Clark Street
Chicago, IL 60504
(312) 353-9317

Albert H. Adelman
ENSR Consulting and Engineering
696 Virginia Road
Concord, MA 01742

David B. Agus
University of Pennsylvania School of Medicine
4418 Spruce Street, Apt. E-1
Philadelphia, PA 19104
(215) 222-2324

E. N. Amick
Lockheed - ESC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89199
(702) 734-3287

William C. Anderson
IT Corporation
312 Directors Drive
Knoxville, TN 37923
(615) 690-3211

J. Andrade
College of Engineering - MEB
University of Utah
Salt Lake City, UT 84112
(801) 581-4379

W. F. Arendale
Chemistry Department
University of Alabama
Huntsville, AL 35899
(205) 895-6473

Neil Arnold
Center for Micro Analysis
University of Utah
214 EMRL Building 61
Salt Lake City, UT 84112
(801) 581-8431

Russell Arnold
Food and Drug Administration
5600 Fishers Lane
Rockville, MD 20857
(301) 443-2872

Tad Bacon
Environ. Analytical Systems, Inc.
1400 Taylor Avenue
P.O. Box 9840
Baltimore, MD 21284-9840
(301) 321-5133

Harold Balbach
U.S. Army CERL
P.O. Box 4005
Champaign, IL 61820-1305
(217) 373-7251

Karen Bankert
USEPA Region IX (P-3-2)
215 Fremont Street
San Francisco, CA 94105
(415) 974-8856

John Barich
USEPA, Region X
1200 6th Avenue
Seattle, WA 98101
(206) 442-8562

M. H. Bartling
Lockheed - EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Raymond J. Bath
NUS Corporation
1090 King Georges Post Highway
Edison, NJ 08837
(201) 225-6160

Tom Baugh
USEPA
401 M Street SW
Washington, DC 20460
(202) 382-5798

G. R. Bear
Shell Development Company
P.O. Box 1380
Houston, TX 77001
(713) 493-8024

Werner Beckert
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2137

Marian Bedinger
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2372

Participants' List - continued

Joseph V. Behar
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2203

Bob Beimer
S-CUBED
P.O. Box 1620
La Jolla, CA 92038
(619) 453-0060

Henry Beiro
Martin Marietta Energy Systems
P.O. Box 2003, M.S. 7440
Oak Ridge, TN 37831
(615) 576-1568

Walter Berger
Enseco, Inc.
7440 Lincoln Way
Garden Grove, CA 92641
(213) 598-0458

Richard E. Berkley
USEPA - MD-44
Research Triangle Park, NC 27711
(919) 541-2439

Bob Berkshire
U.S. Army Environmental Hygiene Agency
Aberdeen Proving Ground, MD
21010-5422
(301) 671-2208/3739

Bernie B. Bernard
O.I. Corporation
P.O. Box 2980
College Station, TX 77841-2980
(409) 690-1711

John Berthold
Babcock & Wilcox Company
1562 Beeson Street
Alliance, OH 44601
(216) 821-9110, ext. 271

Don Betowski
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2116

Stephen Billets
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2232

Tracie L. Billington
California Dept. of Health Services
83 Scripps Drive
Sacramento, CA 95825
(916) 924-2139

Hari Bindal
U.S. Air Force
HQ AFSC/DEV
Andrews Air Force Base, MD 20334
(301) 981-6341

Michael Birch
USEPA, Region IV
College Station Road
Athens, GA 30613
(404) 546-2447

Reginia Bochicciho
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2150

William Bokey
USEPA - Hazardous Waste Section
College Station Road
Athens, GA 30613
(404) 546-3357

David Bottrell
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2142

Wayne Boyles
Hach Company
P.O. Box 389
Loveland, CO 80539
(393) 669-3050 ext. 2246

Julie L. Bozich
USEPA, Region VI (6H-EC)
1445 Ross Avenue
Dallas, TX 75202
(214) 655-6730

George Brilis
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2112

Peter Brown
Leeman Labs Inc.
600 Suffolk Street
Lowell, MA 01854
(617) 454-4442

William Brumley
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2684

Randy Bryson
Brunswick Defense
9509 International Court North
St. Petersburg, FL 33716
(813) 576-5482

Rod Bushway
Department of Food Science
University of Maine
102 B. Holmes Hall
Orono, ME 04469
(207) 581-1626

Larry Butler
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2114

K. J. Cabble
Lockheed-EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Roy Cameron
Lockheed-EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

D. Cardenas
Lockheed-EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Chris Carlsen
Lockheed
1050 E. Flamingo Road, Suite 124
Las Vegas, NV 89119
(702) 734-3258

John M. Carlson
USEPA - Environmental Services Division
60 Westview Street
Lexington, MA 02173

Thomas Carlson - Environmental Systems
Corporation
200 Tech Center Drive
Knoxville, TN 37912
(615) 688-7900

Michael Carrabba
EIC Laboratories Inc.
111 Downey Street
Norwood, MA 02062
(617) 769-9450

Hunt Chapman
Ecology & Environment
1700 N. Moore Street, Suite 1105
Arlington, VA 22209
(703) 522-6065

David Charters
USEPA - Environmental Response Team
Edison, NJ 08873
(210) 906-6825

Doug Chatham
NUS Corporation
1927 Lakeside Parkway, Suite 614
Tucker, GA 30084
(404) 938-7710

P. K. Chattopadhyay
Ecology & Environment, Inc.
160 Spear Street, Suite 1400
San Francisco, CA 94105
(415) 777-2811

Rob Cherney
Hewlett-Packard
1421 S. Manhattan Avenue
Fullerton, CA 92631
(714) 758-5524

T. Lloyd Chesnut
Ohio University
306 Cutler Hall
Athens, OH 45701
(614) 593-2581

Tom Chiang
Lockheed
1050 E. Flamingo Road
Las Vegas, NV 89119
(702) 798-2145

Stan Christensen
ICF Technology
P.O. Box 280041
Lakewood, CO 80228-2213
(303) 236-7414

Wayne Chudyk
Tufts University
Civil Engineering Department
Anderson Hall
Medford, MA 02155
(617) 381-3211

William Claytor
Bruker Instruments, Inc.
19 Fortune Drive
Billerica, MA 01821
(508) 667-9580

Scott Clifford
USEPA, Region I
60 Westview Street
Lexington, MA 02173
(617) 860-4300

William Cole
Lockheed - ESC
1050 E. Flamingo Road, Suite 126
Las Vegas, NV 89119
(702) 734-3226

Stuart P. Cram
Hewlett-Packard
MS-20 BAE
3000 Hanover Street
Palo Alto, CA 94304

Participants' List - continued

Alan B. Crockett
EG & G Idaho
P.O. Box 1625
Idaho Falls, ID 83415-2213
(208) 526-1574

Tom A. Cronk
Oak Ridge National Laboratory
P.O. Box 2567
Grand Junction, CO 81502
(303) 242-8621 ext. 212

Beneta Culpepper
U.S. Analytical Instruments
1511 Industrial Road
San Carlos, CA 94070
(415) 595-8200

John Curtis
Lockheed - ESC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3257

Dileep K. Dandge
ST & E, Inc.
1214 Concannon Boulevard
Livermore, CA 94550
(415) 449-8516

Betty Anne Deason
Lockheed - EMSCO
1050 E. Flamingo Road
Las Vegas, NV 89119
(702) 798-2227

Carla Dempsey
USEPA - OERR
401 M Street SW, Mail Code OS230
Washington, DC 20460
(202) 382-5746

Jane E. Denne
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2655

Gabriel Dib
IT Corporation
4585 Pacheco Boulevard
Martinez, CA 94553
(415) 372-9100

Randall K. Dickinson
United Engineers
30 S. 17th Street
Philadelphia, PA 19101
(215) 422-4987

Chuck Dittmar
Groundwater Technology
24168 Haggerty Road
Farmington Hills, MI 48024
(313) 471-2031

Joseph J. DLugosz
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2598

D. Dobb
Lockheed-EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

J.R. Donnelly
Lockheed
1050 E. Flamingo Road
Las Vegas, NV 89119
(702) 798-2299

Doug Dowis
Arizona Instrument
P.O. Box 336
Jerome, AZ 86331
(602) 634-4263

Brian Dozier
Reynolds Electrical & Engineering Co., Inc.
P.O. Box 98521 M/S 738
Las Vegas, NV 89193-8521
(702) 295-6879

Jo Ann Duchene
ICAIR-Life Systems Inc.
24755 Highpoint Road
Cleveland, OH 44122
(216) 464-3291

Peter H. Duquette
Bio-Metric Systems, Inc.
9924 West Seventy-Fourth Street
Eden Prairie, MN 55344
(612) 829-2714

Philip Durgin
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2623

F. F. Dyer
Martin Marietta Energy Systems
Oak Ridge National Laboratory
P.O. Box 2008 Building 4500S
MS-6128
Oak Ridge, TN 37831-6128
(615) 574-6856

David G. Easterly
USEPA
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2108

DeLyle Eastwood
Lockheed - ESCO
1050 E. Flamingo Road, Suite 208
Las Vegas, NV 89119
(702) 734-3287

Participants' List - continued

Lawrence Eccles
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2385

V. A. Ecker
Lockheed - EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

John Edwards
Avalon Ventures III
c/o Ms. Alexis Parks
973 Fifth Avenue
Boulder, CO 80302
(303) 443-7010

Van Ekambaram
Woodward - Clyde Consultants
4582 S. Ulster Street, Suite 1000
Denver, CO 80237
(303) 694-2770

Dudley Emer
Reynolds Electrical & Engineering Co., Inc.
P.O. Box 98521 M/S 738
Las Vegas, NV 89193-8521
(702) 295-6879

Ed Eschner
Lockheed
1050 E. Flamingo Road
Las Vegas, NV 89121
(702) 734-3508

Eugene Esplain
Navajo Nation Superfund Office
P.O. Box 2946
Window Rock, AZ 86515
(602) 871-5772

Joan Etheridge
Ontario Waste Management Corp.
845 Harrington Court
Burlington, Ontario
CANADA L7N3P3
(416) 637-2452

Harold Ethridge
Louisiana Dept. of Environ. Quality
625 N. 4th Street
Baton Rouge, LA 70802
(504) 342-8925

John C. Evans
Battelle Pacific Northwest Laboratories
P.O. Box 999/ MSIN; K6-81
Richland, WA 99352
(509) 376-0934

Louis Feige
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2226

I. Cecil Felkner
Technical Assessment Systems, Inc.
1000 Potomac Street NW
Washington, DC 20007
(202) 337-2625

Bruce S. Ferguson
ImmunoSystems Inc.
8 Lincoln Street
P.O. Box AY
Biddeford, ME 04005
(207) 282-4146

Mario Fernandez, Jr.
U.S. Geological Survey
4710 Eisenhower Boulevard, Suite B5
Tampa, FL 33634
(813) 228-2124

Carlos Alberto Ferreira
CETESB-CIA De Technologia De
Saneamento Ambiental
Av. Itambe, 38 - Sta. Luzia
Taubate, Sao Paulo
BRAZIL CEI 12100
0122-33-4900

Thomas L. Ferrell
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6123
(615) 574-6214

James H. Ficken
U.S. Geological Survey
Building 2101
Stennis Space Center, MS 39529
(601) 688-1548

Stephen R. Finch
Dexsil Corporation
One Hamden Park Drive
Hamden, CT 06517
(203) 288-3509

Stanley Finger
Vitreous State Lab
Catholic University
Washington, DC 20046
(202) 259-6711

Robert Finnigan
Finnigan Corporation
355 River Oaks Parkway
San Jose, CA 95134
(408) 433-4800

Timothy L. Fisher
U.S. Army Environ. Hygiene Agency
HSHB-ML-A/Analytical QA Office
Aberdeen Proving Ground, MD
21010-5422
(301) 671-3269

Participants' List - continued

Joan Fisk
USEPA - OERR
401 M Street SW (OS 230)
Washington, DC 20460
(202) 382-3115

Donald A. Flory
Flory Environmental Consultants, Inc.
3214 Churchill
Pearland, TX 77581
(713) 485-3603

Mike Franz
Enseco, Inc
7440 Lincoln Way
Garden Grove, CA 92641
(213) 598-6458

Doug Frazer
USEPA, Region X
215 Fremont Street
San Francisco, CA 94105
(415) 485-1228

Scott Fredericks
USEPA
401 M Street SW
Washington, DC 20460
(202) 475-8103

William W. Freeman
Roy F. Weston, Inc.
Weston Way
West Chester, PA 19380
(215) 344-3616

David Friedman
USEPA - Office of Solid Waste
401 M Street, SW
Washington, DC 20460
(202) 382-4761

David Gahr
Lockheed - ESC
1050 E. Flamingo Road
Las Vegas, NV 89119
(702) 734-3292

Richard B. Gammage
Oak Ridge National Laboratory
P.O. Box 2008, Building 7509
MS 6383
Oak Ridge, TN 37831-6383
(615) 574-6256

Gomes Ganapathi
Bechtel National, Inc.
800 Oak Ridge Turnpike
Oak Ridge, TN 37837
(615) 572-7102

Steven P. Gardner
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2580

Clare Gerlach
Lockheed
1050 E. Flamingo Road
Las Vegas, NV 89119
(702) 798-2227

Jacob Gibs
U.S. Geological Survey
810 Bear Tavern Road
West Trenton, NJ 08628
(609) 771-3900

H. K. Gibson
IT Corporation
5815 Middlebrook Pike
Knoxville, TN 37921
(615) 588-6401

Greg Gillispe
Dept. of Chemistry
North Dakota State University
Fargo, ND 58105
(701) 237-8244

Richard K. Glanzman
CH2M Hill
6060 South Willow Drive
P.O. Box 22508
Denver, CO 80222
(303) 771-0900

Dick A. Glass
E-N-G Mobile Systems, Inc.
2950 Cloverdale Avenue
Concord, CA 94518
(415) 798-4060

Garth Glenn
NUS Corporation
999 West Valley Rd.
Wayne, PA 19087
(215) 687-9510

Donald E. Glowe
Texas Research Institute
9063 W. Bee Caves Road
Austin, TX 78733
(512) 263-2101

Bruce Godfrey
Curtis & Tompkins Labs
2323 Fifth Street
Berkeley, CA 94710
(415) 486-0900

Steven C. Goheen
Battelle, Pacific Northwest Laboratories
P.O. Box 999
Richland, WA 99352
(509) 376-3286

Larry Golden
CAE Instrument Rental
207 N. Woodwork Lane
Palatine, IL 60067
(312) 991-3300

Participants' List - continued

John L. Gordon
North American Weather Consultants
3761 South 700 East
Salt Lake City, UT 84106
(801) 263-3500

Kisholoy Goswami
ST & E, Inc.
1214 Concannon Boulevard
Livermore, CA 94550
(415) 449-8516

Thomas E. Gran
ETC - Findlay Laboratory
P.O. Box 1404
16406 U.S. Route 224 E.
Findlay, OH 45858
(419) 424-4925

Doug Grant
Geraghty & Miller, Inc.
P.O. Box 273630
Tampa, FL 33688-3630
(813) 961-1921

Robert Grant
V. G. Gas Analysis Systems
Aston Way, Middlewich
ENGLAND CW10 OHT
+44 60684 4731

Robin Grant
Lockheed - ESC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89117
(702) 734-3255

Daniel Greathouse
USEPA - Risk Reduction Engineering
26 W. Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7885

Mark Greene
University of Pennsylvania School of Medicine
4418 Spruce Street, Apt. E-1
Philadelphia, PA 19104
(215) 222-2324

Donald Gregonis
Albion Instruments
4745 Wiley Post Way
650 Plaza 6
Salt Lake City, UT 84116
(801) 364-2021

Alan Grey
EG & G Idaho, Inc.
P.O. Box 1625
Idaho Falls, ID 83415
(208) 526-1414

Peter Grohse
Research Triangle Institute
Research Triangle Park, NC 27709
(919) 541-6897

Deborah Gustowski-Gatto
Institute for Environmental Studies
Louisiana State University
Room 42 Atkinson Hall
Baton Rouge, LA 70803
(504) 388-4290

J. W. Haas, III
Martin Marietta Energy Systems
Oak Ridge National Laboratory
P.O. Box 2008, Mail Stop 6114
Building 4500S
Oak Ridge, TN 37831-6113
(615) 576-7607

Michael C. Hadka
W. B. Satterthwaite Associates
720 N. Five Points Road
West Chester, PA 19380
(215) 692-5770

Andrew Hafferty
Ecology & Environment
101 Yesler Way
Seattle, WA 98104
(206) 624-9537

Patrick L. Hammack
U.S. Environmental Protection Agency
1445 Ross Avenue
Dallas, TX 75202
(214) 655-2270

Frank Hammer
Finn Sugar Biochemicals
1400 N. Meacham Road
Schaumburg, IL 60173-4808
(312) 843-3200

Barbara L. Hanby
Hanby Analytical Laboratories, Inc.
4400 South Wayside, Suite 107
Houston, TX 77087
(713) 649-4500

John Hanby
Hanby Analytical Laboratories Inc.
4400 South Wayside, Suite 107
Houston, TX 77087
(713) 649-4500

Robert C. Hanisch
Enseco Corporation
4955 Yarrow Street
Arvada, CO 80002
(303) 421-6611

Ken Hanks
Arizona Dept. Environ. Quality
2005 N. Central Avenue
Phoenix, AZ 85004
(602) 257-2394

Participants' List - continued

Philip Hanst
Infrared Analysis, Inc.
11 Ganung Drive
Ossining, NY 10562
(914) 762-6975

Tony Harding
Tracor Xray
305 W. Magnolia #321
Ft. Collins, CO 80526
(303) 491-7712

Rita M. Harrell
NSI Technology Services Corporation
P.O. Box 12313
2 Triangle Drive
Research Triangle Pk., NC 27709
(919) 541-5387

Keith Harris
Grundfos Pumps
2555 Clovis Avenue
Clovis, CA 93612
(209) 292-8000 ext 302

Robert O. Harrison
Department of Entomology
University of California
Davis, CA 95616
(916) 752-5109/6571

Christopher G. Harrod
ENSR Consulting & Engineering
740 Pasquinelli Drive, Suite 124
Westmont, IL 60559
(312) 887-1700

Don Hartman
Hach Company
P.O. Box 389
Loveland, CO 80539
(303) 669-3050 ext. 2246

Scott Hazard
Lockheed - ESC
1050 E. Flamingo Road
Las Vegas, NV 89119
(702) 736-8884

Edward Heithmar
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2626

John R. Helvig
USEPA, Region VII
Air Monitoring Section
Environmental Services Division
25 Funston Road
Kansas City, KS 66115
(913) 236-3884

Robert Hemeroth
Arizona Dept. of Health Services
1520 West Adams Street
Phoenix, AZ 85007
(602) 255-1188

Charles B. Henry
Institute for Environmental Studies
Louisiana State University
42 Atkinson Hall
Baton Rouge, LA 70803
(504) 388-8521

Stephen C. Hern
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2203

Nelson Herron
Lockheed - ESC
1050 E. Flamingo Road, Suite 126
Las Vegas, NV 89119
(702) 798-2176

A. Judson Hill
Westinghouse Bioanalytic Systems Company
15225 Shady Grove Road, Suite 306
Rockville, MD 20850
(301) 670-0688

D. Hillman
Lockheed - EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Lance Hines
U.S. Army Engineer District Omaha
1624 Douglas Street No. 320
Omaha, NE 68102
(402) 221-7868

Thomas Hinners
USEPA - Environmental Monitoring Systems Lab.
P.O., Box 93478
Las Vegas, NV 89193-3478
(702) 798-2140

Raymond H. Hirshman
Arizona Dept. of Health Services
Division of State Laboratory Services
1520 W. Adams
Phoenix, AZ 85007
(602) 255-1188

James S. Ho
USEPA - Environmental Monitoring and
Systems Lab.
26 W. Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7321

Participants' List - continued

Paul A. Hodakievic
Technology Applications, Inc.
26 W. Martin Luther King Drive
Cincinnati, OH 45268
(513) 569-7321

Michael T. Homsher
Lockheed - ESC
1050 E. Flamingo Road, Suite 246
Las Vegas, NV 89119
(702) 734-3312

Richard Horne
Ecology and Environment Inc.
1509 Main Street, Suite 1400
Dallas, TX 75201
(214) 742-6601

Sarah Horowitz
BP Research International Research Center
4440 Warrensville Center Road
Cleveland, OH 44128
(216) 581-5284

John Hosenfeld
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110
(816) 753-7600

Marilyn Hoyt
ENSR Consulting & Engineering
696 Virginia Road
Concord, MA 01742
(508) 369-8910

Alissa Hudson
CHEMetrics, Inc.
Route 28
Calverton, VA 22016
(703) 788-9028

Tom Huetteman
USEPA Region IX (P-3-2)
215 Fremont Street
San Francisco, CA 94105
(415) 974-0923

David Hulst
Hulst Research Farm Services
4449 Tully Road
Hughson, CA 95326
(209) 883-2164

Alan Humphrey
USEPA - Environmental Response Team, Bldg 10
Woodbridge Avenue
Edison, NJ 08837
(201) 321-6748

Michael L. Hurd
USEPA - Analytical Operations Branch
401 M Street SW
Washington, DC 20460
(202) 382-7906

Rick Irvin
Engineering Toxicology Division
Texas A&M University
College Station, TX 77843
(409) 845-0731

Elizabeth Jangula
Arizona State Laboratory
1520 W. Adams
Phoenix, AZ 85007
(602) 255-1188

Lynn Jarvis
Microsensor Systems, Inc.
5610 Sandy Lewis Drive
Fairfax, VA 22032
(703) 323-0034

Stephen Jensen
Curtis & Tompkins, Ltd.
2323 Fifth Street
Berkeley, CA 94710
(415) 486-0900

Janine Jessup
Idaho National Engineering Lab.
P.O. Box 1625 CFA 633
Idaho Falls, ID 83415-4123
(208) 526-4541

Roy R. Jones
USEPA, Region X
1200 6th Avenue ES 096
Seattle, WA 98101
(206) 442-7373

Tammy Jones
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2144

Bill Jow
Groundwater Technology Environmental
Laboratories
20610 Manhattan Place, Suite 108
Torrance, CA 90501
(213) 328-7959

Freia Jung
University of California
Department of Entomology 0420
Davis, CA 95616
(916) 752-5109

Edward J. Kantor
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2690

Philip A. Keith
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 71825
Las Vegas, NV 89170-1825
(702) 734-3207

Participants' List - continued

Johnathan Kenny
Department of Chemistry
Tufts University
62 Talbot Avenue
Medford, MA 02155
(617) 381-3397

H. B. Kerfoot
Lockheed - ESC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3257

Suhas N. Ketkar
Extrel Corporation
240 Alpha Drive
Pittsburgh, PA 15238
(412) 963-7530

William Kilgore
California Dept. of Health Services
83 Scripps Drive
Sacramento, CA 95825
(916) 924-2599

Trude V. V. King
U.S. Geological Survey
P.O. Box 25046
Denver, CO 80225
(303) 236-1373

Stanley M. Klainer
ST & E, Inc.
1214 Concannon Boulevard
Livermore, CA 94550
(415) 449-8516

Robert D. Kleopfer
Hall-Kimbrell Environ. Services Inc.
4747 Troost
Kansas City, MO 64110
(816) 756-3162

Bonnie Koch
Navajo Superfund Office
P.O. Box 2946
Window Rock, AZ 86515
(602) 871-5772

Thomas Koch
Maryland Medical Laboratory, Inc.
1901 Sulphur Spring Road
Baltimore, MD 21227
(301) 247-9100

Eric N. Koglin
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2432

John Koutsandreas
USEPA (RD-680)
401 M Street SW
Washington, DC 20460
(202) 382-5789

Pat Kraker
ICF Technology
P.O. Box 280041
Lakewood, CO 80228-2213
(303) 236-7414

Lisa Kulju
NUS Corporation
19 Crosby Drive
Bedford, MA 01730
(617) 275-2970

Narindar Kumar
USEPA, Region IV
345 Courtland Street
Atlanta, GA 30365
(404) 347-5065

William Lacy
CDM Federal Programs Center
13135 Lee Jackson Memorial Highway No. 200
Fairfax, VA 22033
(703) 968-0900

G. Laing
Lockheed - EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Myron Douglas Lair
USEPA - Hazardous Waste Section
College Station Road
Athens, GA 30613-7799
(404) 546-3351

Victor Lambou
USEPA
5320 Eugene Avenue
Las Vegas, NV 89108
(702) 759-2259

Frank Laukien
Bruker Instruments, Inc.
19 Fortune Drive
Billerica, MA 01821
(508) 667-9580

Tim Launius
Roy F. Weston, Inc.
5820 Lilley Road
Canton, MI 48187

Vernon J. Laurie
USEPA (RD-680)
401 M Street SW
Washington, DC 20460
(202) 382-5795

Eugene Leach
Caterpillar
100 N E Adams Street JB 3330
Peoria, IL 61629
(309) 675-1329

Participants' List - continued

Gary Lee
Microsenser Technology Inc.
41762 Christy Street
Fremont, CA 94538
(415) 490-0900

Roger W. Lee
USGS-WRD
801 Broadway
Nashville, TN 37203
(615) 736-5424

T. L. Lewis
Lockheed
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3287

Albert A. Liabastre
U.S. Army Environ. Hygiene Agency
Building 180
Ft. McPherson, GA 30330-5000

Russell Lidberg
Lockheed - ESCO
1050 E. Flamingo Road, Suite 208
Las Vegas, NV 89119
(702) 734-3287

Mark Lieber
ICF Technology
9300 Lee Highway
Fairfax, VA 22031
(703) 934-3000

Daniel Lillian
USEPA, Region II
Environmental Services Division
Woodbridge Avenue
Edison, NJ 08837
(201) 321-6707

Thomas Limero
Krug International
1290 Hercules Drive, Suite 120
Houston, TX 77058
(713) 483-8442

A. Linenberg
Sentex Sensing Technology Inc.
553 Broad Avenue
Ridgefield, NJ 07657
(201) 945-3694

Viorica Lopez-Avila
Acurex Corporation
485 Clyde Avenue
Mountain View, CA 94039
(415) 961-5700

Alec Loudon
Bruker Instruments, Inc.
19 Fortune Drive
Billerica, MA 01821
(508) 667-9580

Norman Low
Hewlett-Packard
1601 California Avenue
Palo Alto, CA 94304
(415) 857-7381

Nile Luedtke
Martin Marrietta - Energy Systems
P.O. Box 2003
Oak Ridge, TN 37831
(615) 574-8752

Marianne L. Lynch
VIAR and Company
209 Madison Street
Alexandria, VA 22314
(703) 684-5678

Patricia Mack
USEPA, Region IX
944 E. Harmon
Las Vegas, NV 89119
(702) 798-2250

Philip Malley
Lockheed - ESC
1050 E. Flamingo Road, Suite 124
Las Vegas, NV 89119
(702) 734-3207

Charles K. Mann
Department of Chemistry
Florida State University
Tallahassee, FL 32306
(904) 644-3747

Joanne Manygoats
Navajo Superfund Program
P.O. Box 2946
Window, AZ 86515
(602) 871-5772

Chung-Rei Mao
Corps of Engineers
12565 W. Center Road
Omaha, NE 68144-3869
(402) 221-7494

Leslie Maple
CHEMetrics, Inc.
Route 28
Calverton, VA 22016
(703) 788-9028

Mark Marcus
Chemical Waste Management, Inc.
150 W. 137th Street
Riverdale, IL 60627
(312) 841-8360

Robert Marguccio
Ecology and Environment
1509 Main Street, Suite 1500
Dallas, TX 75201
(214) 742-6601

Participants' List - continued

Paul Marsden
S-CUBED
3398 Carmel Mt. Road
San Diego, CA 92126
(619) 453-0060

John Marshall
HNU Systems, Inc.
160 Charlemont Street
Newton, MA 02161
(617) 964-6690

Joseph D. Mastone
Roy F. Weston, ESAT Division
Landmark One
One Vande de Graaff Drive
Burlington, MA 01803
(617) 229-2050

Cindy L. Mayer
Lockheed - ESC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3257

Aldo T. Mazzella
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2254

Russell McCallister
ICF, Inc.
9300 Lee Highway
Fairfax, VA 22031-1207
(703) 934-3909

Harry B. McCarty
VIAR and Company
209 Madison Street
Alexandria, VA 22314
(703) 684-5678

William McClenny
USEPA - Environmental Monitoring Systems Lab.
Mail Drop 44
Research Triangle Park, NC 27711
(919) 541-3158

Lisa McKenzie
USEPA, Region IX
944 E. Harmon
Las Vegas, NV 89119
(702) 798-2298

Jack McLaughlin
Ecology and Environment
6440 Hillcroft, Suite 402
Houston, TX 77081
(713) 771-9460

D. McNelis
Environmental Research Center
University of Nevada - LV
Las Vegas, NV 89154
(702) 739-3382

Richard E. Means
NSI Technology Services Corp.
P.O. Box 12313
2 Triangle Drive
Research Triangle Pk, NC 27709
(919) 541-5387

Richard T. Medary
Army Corps of Engineers
601 E. 12th Street
Kansas City, MO 64106-2896
(816) 426-5806

Eugene Meier
USEPA Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2237

Anne Melia
Ecology & Environment Inc.
6405 Metcalf Avenue
Clover Leaf Bldg. 3
Overland Park, KS 66202
(913) 432-9961

Frank J. Messina
USEPA
Woodbridge Avenue
Edison, NJ 08837
(201) 906-6170

Henk Meuzelaar
Center for Micro Analysis
University of Utah
ERML Building 61, Room 214
Salt Lake City, UT 84112
(801) 581-8431

Bryan Miller
Hewlett-Packard Company
5725 West Las Positas Boulevard
Pleasanton, CA 94566
(415) 460-1644

Dennis A. Miller
Lockheed - ESC
1050 E. Flamingo Road
Las Vegas, NV 89119
(702) 798-2376

Gary Miller
Jacobs Engineering
428 S. Quail Street
Lakewood, CO 80226
(303) 232-7093

Larry S. Miller
Battelle
505 King Avenue
Columbus, OH 43201
(614) 424-5316

Gayle F. Mitchell
Civil Engineering Department
Ohio University
Athens, OH 45701 (614) 593-2476

Ronald K. Mitchum
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2103

Bruce Molholt
USEPA, Region III
841 Chestnut (3HW16)
Philadelphia, PA 19107
(215) 597-6682

Patrick Molloy
Navajo Nation Superfund Office
P.O. Box 2946
Window Rock, AZ 86515
(602) 871-5772

Jim Moore
Tracor Xray
345 E. Middlefield Road
Mountain View, CA 94043
(415) 967-0350

Leuren Moret
ST & E, Inc.
1214 Concannon Boulevard
Livermore, CA 94550
(415) 449-8516

Frank A. Morris
Brown and Caldwell Laboratories
1255 Powell Street
Emeryville, CA 94608
(415) 428-2300

W. D. Munslow
Lockheed
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Jack Murphy
IN-SITU, Inc.
P.O. Box I
Laramie, WY 82070
(307) 742-8213

Bohdan Mykijewycz
USEPA, Region III
841 Chestnut Building
Philadelphia, PA 19107
(215) 597-3153

Royal J. Nadeau
USEPA - Environmental Response Team
Woodbridge Avenue
Edison, NJ 07060
(201) 321-6743

Clifford Narquis
BP America
4440 Warrensville Center Road
Cleveland, OH 44128
(216) 581-5252

Charles H. Nauman
USEPA
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2258

William Newberry
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2167

Bruce J. Nielsen
Headquarters Air Force Engineering and
Services Center
HQ AFESC/RDVW
Tyndall AFB, FL 32403-6001
(904) 283-2942

John W. Nixon
Chemical Waste Management
150 W. 137th Street
Riverdale, IL 60627
(312) 841-8360

John M. Nocerino
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2110

Nathan Nunn
Lockheed
1050 E. Flamingo Road, Suite 126
Las Vegas, NV 89119
(702) 798-2171

Jonathan E. Nyquist
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831
(615) 574-4646

R. A. Olivero
Lockheed - EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Khris B. Olsen
Battelle Pacific Northwest Labs.
P.O. Box 999, MSN; K6-81
Richland, WA 99352
(509) 376-4114

Maureen O'Mara
Roy F. Weston, Inc.
111 N. Canal, Suite 855
Chicago, IL 60606
(312) 993-1067

Ed Overton
Institute for Environmental Studies
42 Atkinson Hall
Louisiana State University
Baton Rouge, LA 70803
(504) 388-8521

Participants' List - continued

Jeff Oxenford
AWWA Research Foundation
6666 W. Quincy Avenue
Denver, CO 80235
(303) 794-7711 ext. 6016

Reddy Pakanati
Ecology & Environment
1509 Main Street
Dallas, TX 75201
(214) 742-6601

Joe Paladino
Westinghouse Bioanalytic Systems Company
15225 Shady Grove Road, Suite 306
Rockville, MD 20850
(301) 670-0688

Nancy Parson
Ecology & Environment
717 W. Temple Street
Los Angeles, CA 90012
(213) 481-3870

James R. Pasmore
Columbia Scientific Industries Corp.
P.O. Box 203190
Austin, TX 78720
(512) 258-5191

Selvin Passen
Maryland Medical Laboratory, Inc.
1901 Sulphur Spring Road
Baltimore, MD 21227
(301) 536-1400

Dwight Patterson
Xitech Instruments, Inc.
2919 Burbank Dr.
Fairfield, CA 94533
(707) 425-9283

Brent Payne
Geoscience Consultants, Ltd.
1400 Quail Street, Suite 140
Newport, Beach CA 92660
(714) 724-0536

J. Gareth Pearson
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2203

Randy Perlis
Ecology & Environment, Inc.
1776 S. Jackson Street
Denver, CO 80013
(303) 757-4984

Gary Perryman
USEPA, Region VIII
Building 53 Denver Federal Center
P.O. Box 25366
Denver, CO 80225
(303) 236-5080

Mark Peters
Environmental Research Center
University of Nevada
4505 South Maryland Parkway
Las Vegas, NV 89154-4013
(702) 739-3142

Jimmie D. Petty
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2383

David A. Phillippi
USEPA, Region VII
726 Minnesota Avenue
Kansas City, KS 66101
(913) 236-2836

Ann M. Pitchford
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2203

Albert A. Pleva
New Jersey DEP BPA
65 Prospect Street
Trenton, NJ 08618
(609) 292-7696

Russell H. Plumb, Jr.
Lockheed - ESCO
1050 E. Flamingo Road, Suite 126
Las Vegas, NV 89122
(702) 734-3265

Fred Poeppel
EXTREL
240 Alpha Drive
Pittsburgh, PA 15238
(412) 963-7530

Billy Bob Potter
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-3128

George R. Prince
USEPA - Environmental Response Team
Woodbridge Avenue
Edison, NJ 08837
(201) 321-6649

Thomas H. Pritchett
USEPA - Environmental Response Team
GSA Raritan Depot
Edison, NJ 08829
(201) 321-6738

David Pudvah
VG Instruments, Inc.
32 Commerce Center
Cherry Hill Drive
Danvers, MA 01923
(508) 777-8034

Participants' List - continued

Steven Pyle
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2529

Greg Raab
Lockheed - ESC
1050 E. Flamingo Road, Suite 126
Las Vegas, NV 89119
(702) 734-3332

R. Rajagopal
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2664

Julio Reategui
Environ. Analytical Systems, Inc.
1400 Taylor Avenue
P.O. Box 9840
Baltimore, MD 21284-9840
(301) 321-5133

Joseph Reed
ICF Technology
P O Box 280041
Lakewood, CO 80228-2213
(303) 236-7414

Francis Regina
Allied Signal Corporation
P.O. Box 1021-R
Morristown, NJ 07960
(201) 455-2170

Regina Prevosto Rehm
ICF Technology
P O Box 280041
Lakewood, CO 80228-2213
(303) 236-7414

Les Rice
OI Corporation
P.O. Box 2980
College Station, TX 77841-2980
(409) 690-1711

Albert Robbat
Tufts University
Chemistry Department
Medford, MA 02155
(617) 381-3474

G. L. Robertson
Lockheed - EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Alfredo Carlos Cardoso Rocca
CETESB-CIA Technologia Saneamento Ambiental
R. Agisse 172 AP 81 - Vila Madalena
Sao Paulo, Sao Paulo
BRAZIL 05439
011-210-33-2711

Joseph Roehl
Environ. Anlaytical Systems Inc.
1400 Taylor Avenue
P.O. Box 9840
Baltimore, MD 21284-9840
(301) 321-5304

Joseph F. Roesler
Cincinnati Engineers, Inc.
4030 Mt. Carmel-Tobasco Road
Suite 225
Cincinnati, OH 45255
(513) 528-1888

David Roitman
University of Pennsylvania School of Medicine
4418 Spruce Street, Apt. E-1
Philadelphia, PA 19104
(215) 222-2324

Allen Rosenberg
HNU Systems, Inc.
160 Charlemont Street
Newton, MA 01261
(617) 964-6690

Jeffrey Rosenfeld
Lockheed - ESC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3211

Ronald A. Ross
NSI Technology Services Corporation
Gateway Center, Tower II, Suite 311
4th and State
Kansas City, KS 66101
(913) 281-0307

Mary Ryan
Clean Air Engineering
207 N. Woodwork Lane
Palatine, IL 60067
(312) 991-3300

Mahmoud A. Saleh
Environmental Research Center
University of Nevada
4505 South Maryland Parkway
Las Vegas, NV 89154-4013
(702) 739-3142

Shad M. Sargand
Ohio University
13 Grand Park Boulevard
Athens, OH 45701
(614) 593-1467

Wayne Saunders
ICF Technology, Inc.
9300 Lee Highway
Fairfax, VA 22031
(703) 934-3000

Drew Sauter
A.D. Sauter Consulting
2356 Aqua Vista Avenue
Henderson, NV 89014

Participants' List - continued

John Scalera
USEPA - Central
Central Regional Laboratory
839 Bestgate Road
Annapolis, MD 21401
(301) 266-9180

Douglas T. Scarborough
U.S. Army Toxic and Hazardous Materials Agency
Building E4460 (AMXTH-TE-A)
Aberdeen Proving Ground, MD
21010-5401
(301) 676-7569/671-3348

Kenneth R. Scarbrough
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2645

Eugene Scheide
Environmetrics, Inc.
10679 Midwest Industrial Boulevard
St. Louis, Missouri 63132
(314) 427-0550

Gregory Schiefer
ICAIR-Life Systems Inc.
24755 Highpoint Road
Cleveland, OH 44122
(216) 464-3291

Hendrik Schlesing
biocontrol institut fur chemische und
biologische Untersuchungen
P.O. Box 16 30
6500 Mainz
WEST GERMANY
+6132/2000

Steve Schroedl
Lockheed - ESC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3257

David B. Seielstad
Kevex Corporation
355 Shoreway Road
San Carlos, CA 94070
(415) 591-3600

Jerry L. Sessions
Brunswick Defense
2000 Brunswick Lane
Deland, FL 32724
(904) 736-1700 ext 4352

Mahmoud R. Shahriari
Fiber Optic Center
Rutgers University
Piscataway, NJ 08854
(201) 932-5033

Patricia A. Sheridan
USEPA
GSA Raritan Depot
Woodbridge Avenue
Edison, NJ 08837
(201) 321-6730

Brad Shipley
USEPA, Region IX
215 Fremont Street
San Francisco, CA 94105
(415) 974-8108

Robert Shokes
Science Applications International
Corporation (SAIC)
4224 Campus Pt. Ct.
San Diego, CA 92121
(619) 535-7506

Steven J. Simon
Lockheed - ESC
1050 E. Flamingo Road, Suite 126
Las Vegas, NV 89119
(702) 734-3285

Diann Sims
USEPA - Central Regional Laboratory
839 Bestgate Road
Annapolis, MD 21401
(301) 266-9180

Gary Skiles
Talem Inc.
306 W. Broadway Avenue
Fort Worth, TX 76104
(817) 335-1186

John Skinner
U.S. Environmental Protection Agency
401 M Street, SW
Washington, DC 20460
(202) 382-2600

Amy Smiecinski
Environmental Research Center
University of Nevada
4505 South Maryland Parkway
Las Vegas, NV 89123
(702) 798-3382

Dick Smith
Texas Research Institute
9063 Bee Caves Road
Austin, TX 78733
(512) 263-2101

William P. Smithson
U.S. Army Environmental Hygiene Agency
Aberdeen Proving Ground, MD
21010-5401
(301) 671-2024

Robert N. Snelling
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2525

Charles Soderquist
Enseco Inc.
2544 Industrial Boulevard
West Sacramento, CA 95691
(916) 372-1393

Michael F. Solecki
USEPA - Environmental Response Team
Woodbridge Avenue
Edison, NJ 08837
(201) 906-6918

Lynn Sorensen
Microbics Corporation
2223 Faraday Street, #B
Carlsbad, CA 92008
(619) 438-8282

Joseph Soroka
USEPA, Region II
Woodbridge Avenue
Edison, NJ 08837
(201) 906-6875

G. Wayne Sovocool
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-93478
(702) 798-2212

Lisa Spadini
Marketing Services XRF
Kevex Instruments
355 Shoreway Road
San Carlos, CA 94070
(415) 591-3600

Martin L. Spartz
Dept. of Chemistry, Willard Hall
Kansas State University
Manhattan, KS 66506
(913) 532-6298

Richard D. Spear
USEPA, Region II
Woodbridge Avenue
Edison, NJ 08837
(201) 321- 6685

Thomas M. Spittler
USEPA
60 West View Street
Lexington, MA 02173
(617) 860-4734

Stanford Spurlin
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110
(816) 753-7600

Martin Stapanian
Lockheed - EMSC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Randy St. Germain
Department of Chemistry
North Dakota State University
Fargo, ND 58105
(701) 237-8244

James Stiles
Assessment Systems
7010 Beach Dr. SW, Suite 4
Seattle, WA 98136
(206) 937-8419

Grant Stokes
Geo-Centers Inc.
7 Wells Avenue
Newton Center, MA 02159
(617) 964-7070

Tom Stolzenberg
RMT Inc.
1406 E. Washington Ave, Suite 124
Madison, WI 53711
(608) 255-2134

Michael Story
Finnigan Corporation
355 River Oaks Parkway
San Jose, CA 94134
(408) 433-4800

Hal Stuber
James P. Walsh & Associates, Inc.
P.O. Box 2003
1002 Walnut, Suite 201C
Boulder, CO 80306
(303) 443-3282

Chris Sutton
Ruska Laboratories, Inc.
3601 Dunvale
Houston, TX 77063
(713) 975-0547

Robert Suva
AgriTech Systems Inc.
100 Fore Street
Portland, ME 04101
(207) 774-4334

Melvin J. Swanson
Bio-Metric Systems, Inc.
9924 West 74th Street
Eden Prairie, MN 55344
(612) 829-2700

George Sylvester
Van, Waters, Rogers
1363 South Bonnie Beach
Los Angeles, CA 90023
(213) 265-8122

Participants' List - continued

Michael J. Szezewski
Hewlett-Packard
Rt 41 & Starr Road
Avondale, PA 19311
(215) 268-5444

Andrew P. Szilagyi
ICF Technology Inc.
9300 Lee Highway
Fairfax, VA 22031
(703) 934-3774

Doreen Y. Tai
U.S. Geological Survey
Building 2101
Stennis Space Center, MS 39529
(601) 688-1518

Yoshi Takahashi
Dohrmann Rosemount Analytical Div.
3240 Scott Boulevard
Santa Clara, CA 95054
(408) 727-6000

Charles Tanner
ICAIR-Life Systems
24755 Highpoint Road
Cleveland, OH 44122
(216) 464-3291

Victoria Taylor
TMA/Norcal
2030 Wright Avenue
Richmond, CA 94804
(415) 235-2633

Avraham Teitz
USEPA, Region II
62A Woodbridge Avenue
Highland Park, NJ 08904
(201) 572-6089

Prakash M. Temkar
U.S. Army CERL
Box 4005
Champaign, IL 61820
(217) 373-6747

Francis Thomas
USEPA, Region V
230 S. Dearborn
Chicago, IL 60604
(312) 353-9065

J. Edward Tillman
Target Environmental Services, Inc.
8940-A, Route 108
Oakland Center
Columbia, MD 21045
(301) 992-6622

Kim Titus
Lockheed - ESC
1050 E. Flamingo Road, Suite 212
Las Vegas, NV 89119
(702) 734-3285

Thomas Trainor
Bruker Instruments, Inc.
19 Fortune Drive
Billerica, MA 01821
(508) 667-9580

Jerald D. Trease
U.S. Army Engineer District, Omaha
1624 Douglas Street No. 320
Omaha, NE 68102
(402) 221-7868

Robert Turner
Microsensor Technology
41762 Christy Street
Fremont, CA 94538
(415) 490-0900

J. Vail
ICF Technology Inc.
160 Spear Street No. 1380
San Francisco, CA 94105-1535

Martin Vanderlaan
Lawrence Livermore National Lab.
Biomedical Sciences Division
P.O. Box 5507, L-452
Livermore, CA 94550
(415) 422-5721

J. Jeffrey van Ee
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2203

Jeanette Van Emon
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2203

Anna Vargas
Arizona Dept. Environ. Quality
2005 N. Central Avenue
Phoenix, AZ 85004
(602) 257-6852

David B. Vener
Xontech, Inc.
6862 Hayvenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

Ort Villa
USEPA
839 Bestgate Road
Annapolis, MD 21401
(301) 266-9180

Harold Vincent
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2129

Participants' List - continued

Tuan Vo-Dinh
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831
(615) 574-6249

Rick Vollweiler
Art's Manufacturing & Supply Inc.
105 Harrison
American Falls, ID 83211
(208) 226-2017

Eric A. Wachter
Oak Ridge National Laboratory
P.O. Box 2008, MS 6113
Oak Ridge, TN 37831
(615) 576-2712

Steve Walker
Geraghty & Miller, Inc.
P.O. Box 273630
Tampa, FL 33688-3630
(813) 961-1921

Jim Walsh
James P. Walsh & Associates, Inc.
P.O. Box 2003
1002 Walnut No. 201G
Boulder, CO 80306
(303) 443-3282

Amy Walton
Jet Propulsion Lab.
4800 Oak Grove Drive
Pasadena, CA 91109

Joe Wander
Environmental Services Branch
HQ AFESC/RDVS
Tyndall AFB, FL 32403-6001
(904) 283-4234

Llewellyn Williams
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2203

Dave Wineman
USEPA, Region VI
1440 Ross Avenue
Dallas, TX 75202
(214) 655-6491

Marcus B. Wise
Analytical Chemistry Division
Oak Ridge National Laboratory
P.O. Box 2008, MS 120
Oak Ridge, TN 37831-6120
(615) 574-4867

Hank Wohltjen
Microsensor Systems, Inc.
5610 Sandy Lewis Drive
Fairfax, VA 22032
(703) 323-0034

Steven Wolfe
Ecology & Environment, Inc.
160 Spear Avenue, Suite 1400
San Francisco, CA 94105
(415) 777-2811

Greydon Woolerton
Syprotec Corporation
380 Route No. 1
West Chazy, NY 12992
(800) 361-3652

Ray D. Worden
Ruska Laboratories, Inc.
3601 Dunvale
Houston, TX 77063
(713) 975-0547

John R. Worlund
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2656

Donald T. Wruble
USEPA - Environmental Monitoring Systems Lab.
P.O. Box 93478
Las Vegas, NV 89193-3478
(702) 798-2530

Dwayne Wylie
University of Nebraska
319 Manter Hall
Lincoln, NE 68502
(402) 472-2628

Thomas E. Yeates
USEPA, Region V
Environmental Sciences Division
536 South Clark Street 10th Floor
Chicago, IL 60605
(312) 353-3808

Kaveh Zarrabi
University of Nevada
4505 South Maryland Parkway
Las Vegas, NV 89154
(702) 739-3142

John Zimmerman
Lockheed - ESC
1050 E. Flamingo Road, Suite 120
Las Vegas, NV 89119
(702) 734-3322

Barry Zvibleman
Environmental Instruments
2170 Commerce Avenue, Unit S
Concord, CA 94520
(415) 686-4474